Report No. IITRI U6062-9
(Final Report)

STUDY OF CONVERSION OF FORMALDEHYDE INTO SUGAR-LIKE PRODUCTS

NASA-Ames Research Center,
Moffett Field, California

IIT RESEARCH INSTITUTE

Report No. IITRI U-6062-9
(Final Report)

STUDY OF CONVERSION OF FORMALDEHYDE INTO SUGAR-LIKE PRODUCTS

March 24, 1967 through January 23, 1968

Contract No. Nas2-4184
IITRI PROJECT U6062

Prepared by

Charles H. Riesz

of

IIT RESEARCH INSTITUTE
Technology Center
Chicago, Illinois 60616

for

NASA-Ames Research Center,
Moffett Field, California

Copy No.___

January 23, 1968

FOREWORD

This is Report No. U6062-9 (Final Report) of IITRI Project U6062, Contract No. NAS2-4184, entitled "Study of Conversion of Formaldehyde into Sugar-Like Products." This report covers the period from March 24, 1967, through January 23, 1968.

Personnel who contributed to this project include Dr. J. G. Pritchard, Senior Chemist, and Miss Ann O'Donnell, Assistant Chemist. Dr. Eli. S. Freeman provided administrative direction. The counsel and guidance of Dr. Jacob Shapira, who acted as project monitor for NASA, is gratefully acknowledged. The research was sponsored by the Environmental Control Research Branch, Ames Research Center, Moffett Field, California 94035.

Data are recorded in IITRI Logbooks C17655, C18088 and C17656.

Respectfully submitted,

IIT RESEARCH INSTITUTE

Charles H Riesz

Charles H. Riesz
Senior Chemist
Physical Chemistry Research

Approved by:

E S Freeman

Eli S. Freeman
Assistant Director
Chemistry Research Division

ABSTRACT

STUDY OF CONVERSION OF FORMALDEHYDE INTO SUGAR-LIKE PRODUCTS

The feasibility of synthesis of sugar-like products by γ-irradiation of formaldehyde adsorbed on molecular sieve zeolites has been demonstrated. The conversion and product distribution are dependent upon both the type of zeolite as well as the channel configuration and dimensions. Use of Type A and X zeolites increased the conversion into total product from at least 10 to as much as 1000-times higher than when no matrix was present (paraformaldehyde). A mechanism has been proposed, dependent upon formation of electron hole traps in the zeolites which stabilize free radicals incident to the synthesis. Maximum molecular size is limited by the 11-12Å cavity dimensions of the A and X zeolites. For straight- chain monosaccharides, the largest molecule contains approximately 9-10 carbon atoms. With a decationized zeolite (Zeolon-H), the pores are tunnel-like and the maximum molecular size is not limited. The presence of trapped electrons as well as electron hole traps may also affect the mechanism of synthesis.

TABLE OF CONTENTS

STUDY OF CONVERSION OF FORMALDEHYDE INTO SUGAR-LIKE PRODUCTS

I. INTRODUCTION

Extended manned space missions make reprocessing of biological wastes a trade-off possibility. Within this category, the conversion of carbon dioxide into formaldehyde may be assumed as a probable system. The conversion of formaldehyde into edible food materials then becomes an objective which requires clarification.

The conversion of formaldehyde into sugar-like materials has an impressive history. Condensation into higher molecular weight sugars in the presence of alkaline catalysts was reported by Butlerov[1] in 1861. This early work and almost all additional studies have been concerned with the use of base catalysis. The reaction mechanism proceeds by an aldol-type condensation and is catalyzed by the products of the reaction; addition of glycolic aldehyde and dihydroxyacetone, two initial products, eliminate the induction period which is otherwide observed.[2] Balezin[3] suggested that hydrous calcium oxide not only provides catalysis, but acts as a necessary component of an intermediate in the process. A comprehensive review of the extensive history of this process prepared by Ackerlof and Mitchell,[4] emphasizes the above parameters.

In recent work,[5] the kinetics of the synthesis were studied in detail. In particular, the autocatalytic nature of the formose reaction was confirmed. By use of a back-mixed reactor, partial conversion was achieved. Below 80% conversion, the reaction is temperature-independent with an activation energy approximating zero. Above 80% conversion, the reaction has a high activation energy explained as the result of pyranose and furanose ring formation from straight-chain C-5 and C-6 sugar products. For production of lower aldose and ketose products, e.g., C-3 compounds, need for a less active, more selective catalyst was indicated.

The usual formose is a complex mixture of all possible isomers and steroisomers of C-5 and C-6 aldoses and ketoses. Shapira[5] demonstrated that formose sugar is toxic to weanling rats when fed in amounts greater than 15% of the diet. Thus, restriction of the molecular size and complexity would have inherent advantages for edible uses.

The possible primordial origin of monosaccharides from formaldehyde in the presence of clay minerals has not been demonstrated until recently. Gabel and Ponnamperuma[6] found that naturally occurring aluminosilicates catalyzed the conversion of dilute (10^{-2} M) solutions of formaldehyde at reflux temperatures. In the presence of kaolinite, the conversion of formaldehyde to monosaccharides was over 10% with approximately equal amounts of hexose, pentose and tetrose-triose products. The product distribution at higher concentration (0.33 M) was appreciably changed toward lower molecular weight products.

The concept proposed for this study was based on the above background plus additional information recently developed. First, it was demonstrated that radicals could achieve considerable stability on zeolite surfaces.[7] Methyl radicals, generated by γ-radiation of methane sorbed on Linde Type A zeolite, were stored at 77°K for long periods of time and were identified by e.s.r. spectra. It might be expected that γ-irradiation of formaldehyde would lead to free radicals which, stabilized by the zeolite surface, might recombine in complex fashion to monosaccharide configurations. In contrast, carbon dioxide is not appreciably affected under similar conditions.[8] A second consideration is that the pore size configuration of molecular sieve zeolites should place an upper limit on the molecular size of the condensation product. The surface factor has been cited in selective hydrogenation catalysis.[9,10] In the present feasibility study formaldehyde sorbed on several zeolites was γ-irradiated to provide monosaccharide-like products.

II. EXPERIMENTAL

A. Molecular Sieves

Molecular sieves were received from two sources: Linde Division, Union Carbide Corporation, provided Type A and X products; and Norton Company, Worchester, Mass. 01606, supplied Zeolon-H. Representative structures and information on the various products used are presented in Table 1. All materials

Table 1

MOLECULAR SIEVES

Type	Nominal Pore Diameter Å	Representative Structure
5A	5	$0.75CaO \cdot 0.25Na_2O.Al_2O_3.2SiO_2.xH_2O$
10X	8	$0.75CaO \cdot 0.25Na_2O.Al_2O_3.2SiO_2.xH_2O$
13X	9	$1.00Na_2O.Al_2O_3.2.8SiO_2xH_2O$
Zeolon-H	10	$Na_2O \cdot Al_2O_3.10SiO_2.xH_2O$

were used in pellet form.

B. Procedure

The sieves were activated by heating in dry helium or nitrogen to 500°C for 16 hours prior to use. A portion of the dry sieve was then exposed to dry formaldehyde vapors generated by heating paraformaldehyde (Eastman No. 421) at a slightly elevated temperature (100-125°C). The adsorption could be qualitatively followed by the heat produced. Where the inlet portion appeared to be affected by this heating, this fraction was discarded. Generally, the amount of formaldehyde adsorbed was 10-18% by weight of the sieve; complete saturation was not attempted.

The formaldehyde-sieve material was transferred to a Pyrex vessel, fitted with an internal finger. The Co^{60} source was entered and samples were irradiated at a dose rate of approximately 1.4×10^5 rads/hr; dosimetry was accomplished by standard ferrous sulfate techniques. The exposure was generally longer than 132 hours for the sieves.

Following irradiation, the product was extracted with hot water by means of a Soxhlet extractor. The water-soluble product was acidulated with N/10 sulfuric acid and any calcium sulfate product was removed. The excess sulfate ion was precipitated with a slight excess of barium hydroxide solution. After filtration, carbon dioxide was bubbled through the solution to remove barium ion as barium carbonate. The clear aqueous solution was then evaporated to dryness with a slow stream of air under a slight vacuum at 60°C. The above procedure was not used for the 13X and Zeolon-H sieves, since acidulation produced no precipitate.

Paraformaldehyde After 99.6 g of paraformaldehyde was irradiated for 64 hours, the material was extracted with hot water for about one hour. The extract was evaporated to dryness at 50-60°C under a slight vacuum.

C. Paper Chromatography

Separation of the water-soluble product was accomplished by paper chromatography for the 10X product. Elution with pyridine-water-ethyl acetate produced a series of bands. Development with silver nitrate produced dark colored bands suggestive of the presence of reducing compounds. These products were not further characterized.

D. Gas Chromatography

The comprehensive study of Seeeley et al[11] was used to prepare trimethyl silyl derivatives for evaluation by gas-liquid chromatography. The standard procedure comprised the reaction of approximately 10 mg of dry sample with 0.2 ml of hexamethyldisilazane in the presence of 0.1 ml of trimethylchlorosilane as catalyst, all contained in 1 ml of pyridine solvent under anhydrous conditions. The reagent was obtained in diaphragm-capped bottles from Pierce Chemical Company, Rockford, Illinois 61105, under the trade name, TRI-SIL. The experimental silylations were performed at room temperature in a 1-dram sample vial capped with a silicone septum. Generally, 1-2 hours were allowed for completion of the reaction which occurred at room temperature in the case of standard compounds but at 60-65°C for some of the complex mixtures.

Sweeley et al[11] recommended several packings for accomplishing the separation of the silyl ether derivatives. For a broad spectrum of products, 3% SE-52 (a dimethyl silicone polymer) on Chromasorb (acid-washed and silanized with trimethylchlorosilane) was recommended. The liquid phase was applied by the coating procedure described by Parcher and Urone.[12] This technique utilized fluidization to distribute the SE-52 uniformly on the 80-100 mesh support. An eight-foot column of 0.125-inch O.D. tubing was used.

In the procedure, small samples of the clear solution (disregarding a precipitate which always formed during the preparation) were injected. The samples ranged in size from 0.3 to 0.5 μl (microliters). With a helium flow of 25 ml/min., a hydrogen flow of 25 ml/min. and an air flow of 200-350 ml/min., the initial isothermal column temperature was maintained at 105°C for 0.2 hours; the column was then programmed to rise at the rate of 4°C/min. to 250°C, where isothermal operation was again resumed. The injection port was maintained at 225°C and the flame ionization detector at 270°C. An Aerograph 1520, equipped with flame ionization detection, was used.

Good separation of many monosaccharides through hexose compounds was obtained. Results obtained with pure standards are listed in Table 2. In the analysis of complex product mixtures, it was necessary to correct the analysis for the

Table 2

GAS CHROMATOGRAPHY OF TRIMETHYLSILYL DERIVATIVES OF MONOSACCHARIDES AND RELATED COMPOUNDS

No. of C-Atoms	No. of Active H'S	Compound	Retention Time hrs. x10-1
3	1	Isopropyl alcohol	0.10
4	1	1-Butanol	0.12
2	2	Ethylene glycol	0.23-0.28[a]
3	1	Acetol (hydroxy acetone)	0.31
2	1	Glycolic acid	0.45
3	2	1,3 Propanediol	0.25-0.28[a]
			0.38-0.41[a]
			0.69
3	1	Gylcerine	1.56
2	1	Glycolaldehyde	1.56
5	4	Pentaerythritol	3.42
5	4	L-Arabinose	4.10
4	4	d-Tartaric acid	4.19
5	4	D-Ribose	4.22-4.31[b]
5	4	D-Xylose	4.38
6[c]	4[c]	1,3-Hydroxy,2-propanone[c]	4.69-4.88[a]
6	5	D-Mannose	4.95
6	5	D-Fructose	5.00
6	5	D-Galactose	5.12
6	5	α D-Glucose	5.28
6	5	D-Mannose	5.34
6	6	Sorbitol	5.40
6	5	α, D-Glucose	5.63
9[d]	6[d]	1,3-Hydroxy, 2-propanone[d]	6.16-6.44[a]

---

[a] Doublet peaks. [b] Unresolved doublet. [c] Dimer. [d] Trimer.

presence of solvent-reaction mixture. Thus, both the product and the corresponding unreacted solvent-reaction chromatograms are plotted on the same graph for comparison at identical attenuations.

III. RESULTS

A. 5A Molecular Sieve

The water-soluble products received from irradiation of formaldehyde adsorbed on 5A molecular sieve was 1.5% after 132 hours (Table 3). This can be compared with 0.11% obtained by irradiation of paraformaldehyde. The use of the Type A zeolite matrix has increased the conversion of formaldehyde some 13 times. Use of somewhat arbitrary division points in Figures 1 and 2 based on the calibration of Table 2 permits study of the product distribution.

The primary product formed from formaldehyde irradiation appears to be the pentose materials. This would suggest that the initial reactions might comprise:

$$\gamma\text{-irradiation} + CH_2O \rightsquigarrow CH_2O^* + e \qquad (1)$$

$$CH_2O^* + CH_2O \longrightarrow (CH_2O)_2^* \qquad (2)$$

$$e + (CH_2O)_2^* \longrightarrow (CH_2O)_2 \qquad (3)$$

$$(CH_2O)^*_2 + (CH_2O)_2 \longrightarrow (CH_2O)_4^* \qquad (4)$$

$$(CH_2O)^*_4 + CH_2O \longrightarrow (CH_2O)_5^* \qquad (5)$$

$$e + (CH_2O)_5^* \longrightarrow (CH_2O)_5 \qquad (6)$$

This sequence of events is indicated by the many product peaks appearing in the chromatogram of Figure 1 for paraformaldehyde; a random product distribution is shown by the smooth curves

Table 3

ADSORPTION-IRRADIATION OF FORMALDEHYDE ON MOLECULAR SIEVES

Molecular Sieve	Para-Formaldehyde	5A	10X	13X
Nominal Pore Dia., Å	-	5	8	9
Irradiation Dose rads x 10^7	0.89	1.7	5.3	2.2
Formaldehyde adsorbed %	--	13.0	14.0	14.3
Water-soluble Products, %	0.11	1.5	11.3	11.7
Water-soluble Products, moles/100 moles formaldehyde adsorbed				
C4	0.02	0.09	2.0	2.7
C5	0.06	0.40	3.4	4.2
C6	0.01	0.27	2.3	2.2
Higher	0.02	0.74	3.6	2.6
	0.11	1.50	11.3	11.7
Conversion, moles/100 moles formaldehyde adsorbed				
C4	19	6	18	23
C5	52	27	30	36
C6	13	18	20	19
Higher	16	49	32	22
	100	100	100	100

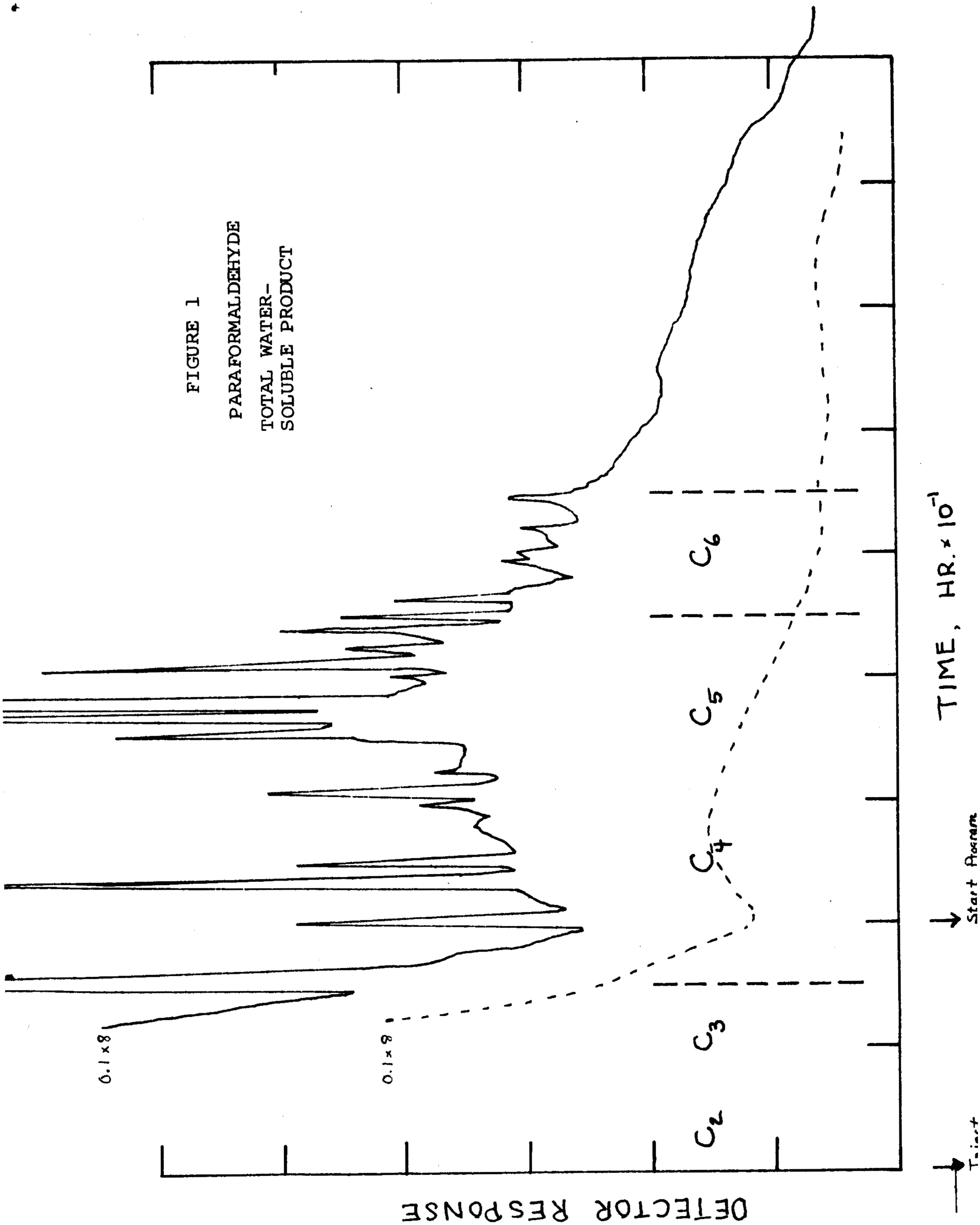


FIGURE 1

PARAFORMALDEHYDE

TOTAL WATER-SOLUBLE PRODUCT

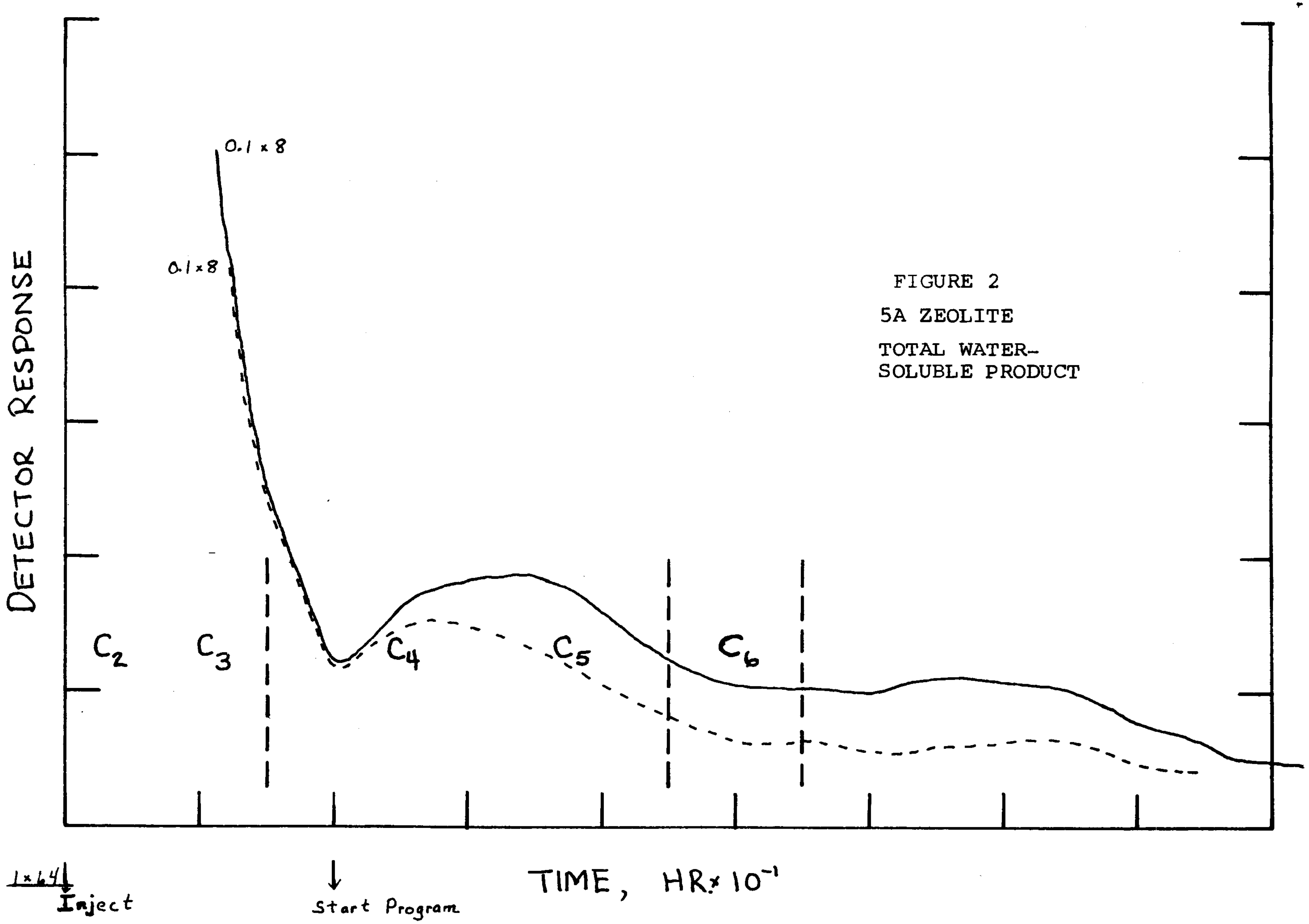


FIGURE 2

5A ZEOLITE

TOTAL WATER-SOLUBLE PRODUCT

of Figure 2 for 5A zeolite product. The $(CH_2O)_2$ above could be an intermediate, glycolaldehyde, which could not be resolved because of the relatively high volatility of this compound in the mixture; its appearance would be obscured by the solvent peak.

B. 10X and 13X Molecular Sieve

Data for 10X and 13X zeolites are presented in Table 3. Gas chromatograms are presented in Figures 3, 4, 5, and 6. The dominant constituents produced a peak in the pentose region as a consequence of reactions depicted above. However, use of these Type X zeolites increased the conversion nearly ten-fold. Along with the formation of this primary product, C-6 and material above C-6 are formed in greater amounts. These secondary decomposition products are induced by extended irradiation which both builds and destroys complex molecules. The adsorption of the compounds on the zeolite surface results in improved stability of both free radicals and products.

C. Zelon-H

The results with Zelon-H are presented in Table 4 along with the data for paraformaldehyde. Whereas the product maximum occurs in the C-5 region for the irradiated paraformaldehyde, the maximum formation of product with Zeolon-H is higher than C-6 (Figure 7). Thus, the nature of the adsorbed species is significantly different with the hydrogen-form of this zeolite. In terms of total formation of products, Zeolon-H is not as effective as 13X, which has generally comparable pore

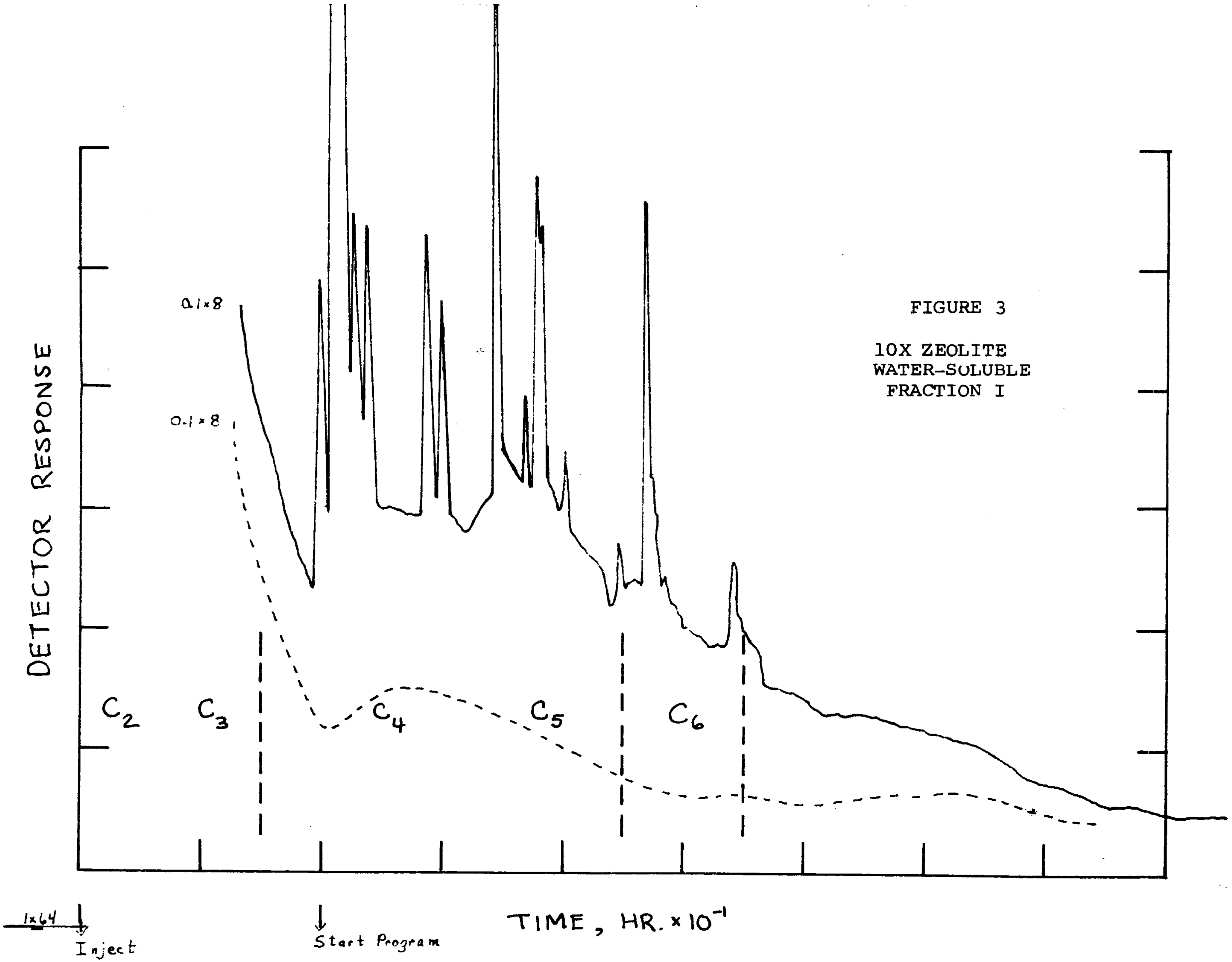
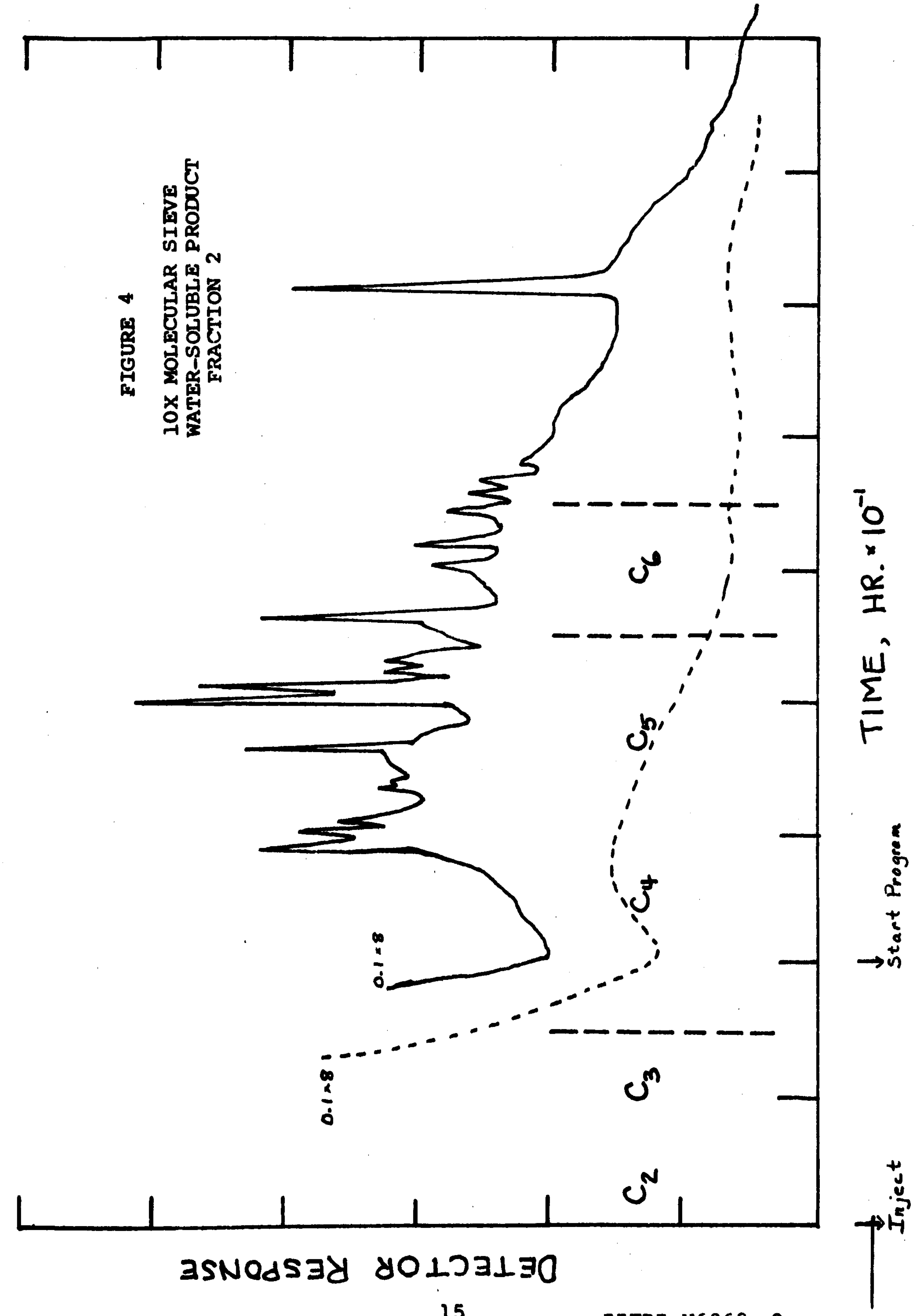


FIGURE 3

10X ZEOLITE
WATER-SOLUBLE
FRACTION I

FIGURE 4

10X MOLECULAR SIEVE
WATER-SOLUBLE PRODUCT
FRACTION 2



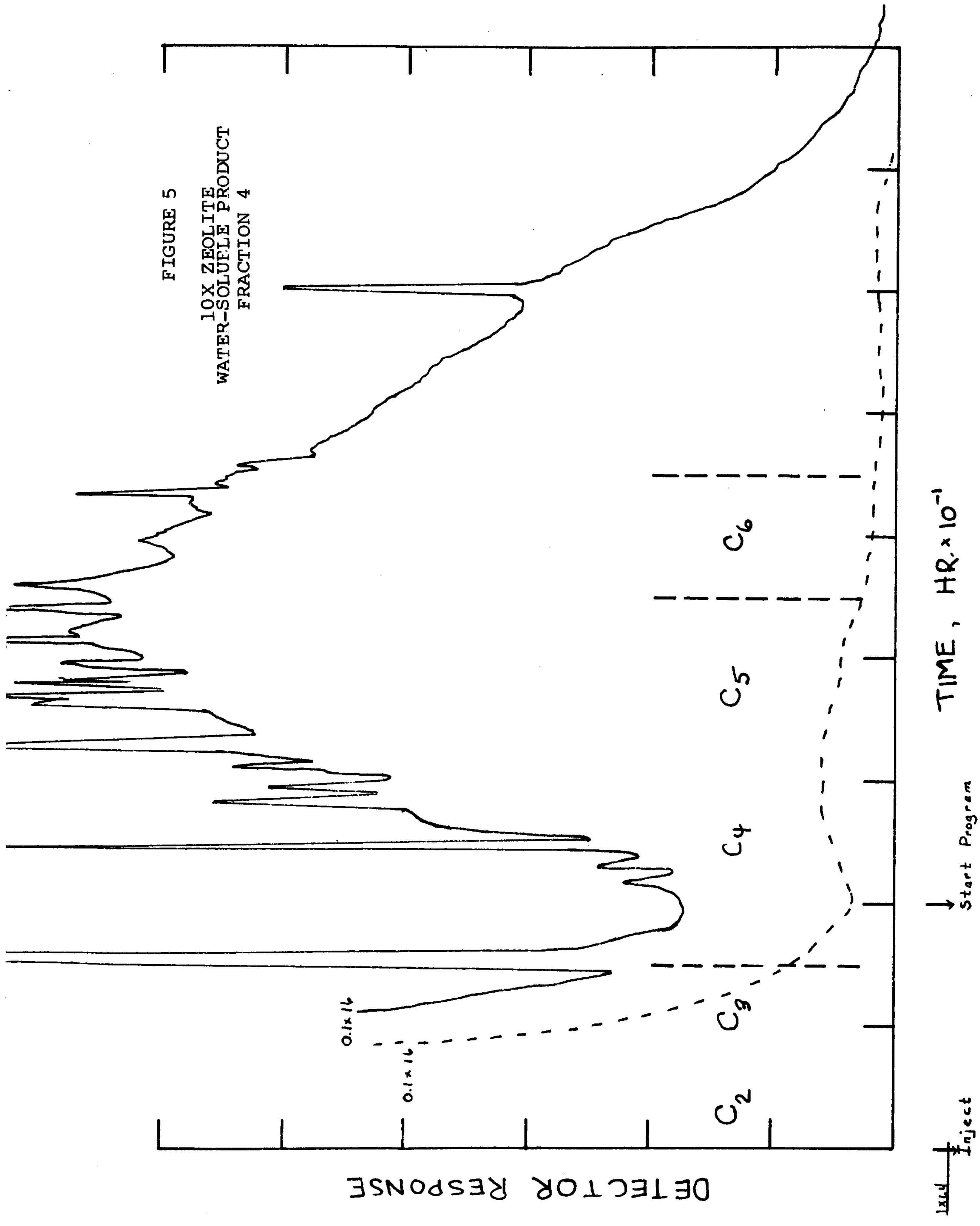


FIGURE 5
10X ZEOLITE
WATER-SOLUBLE PRODUCT
FRACTION 4

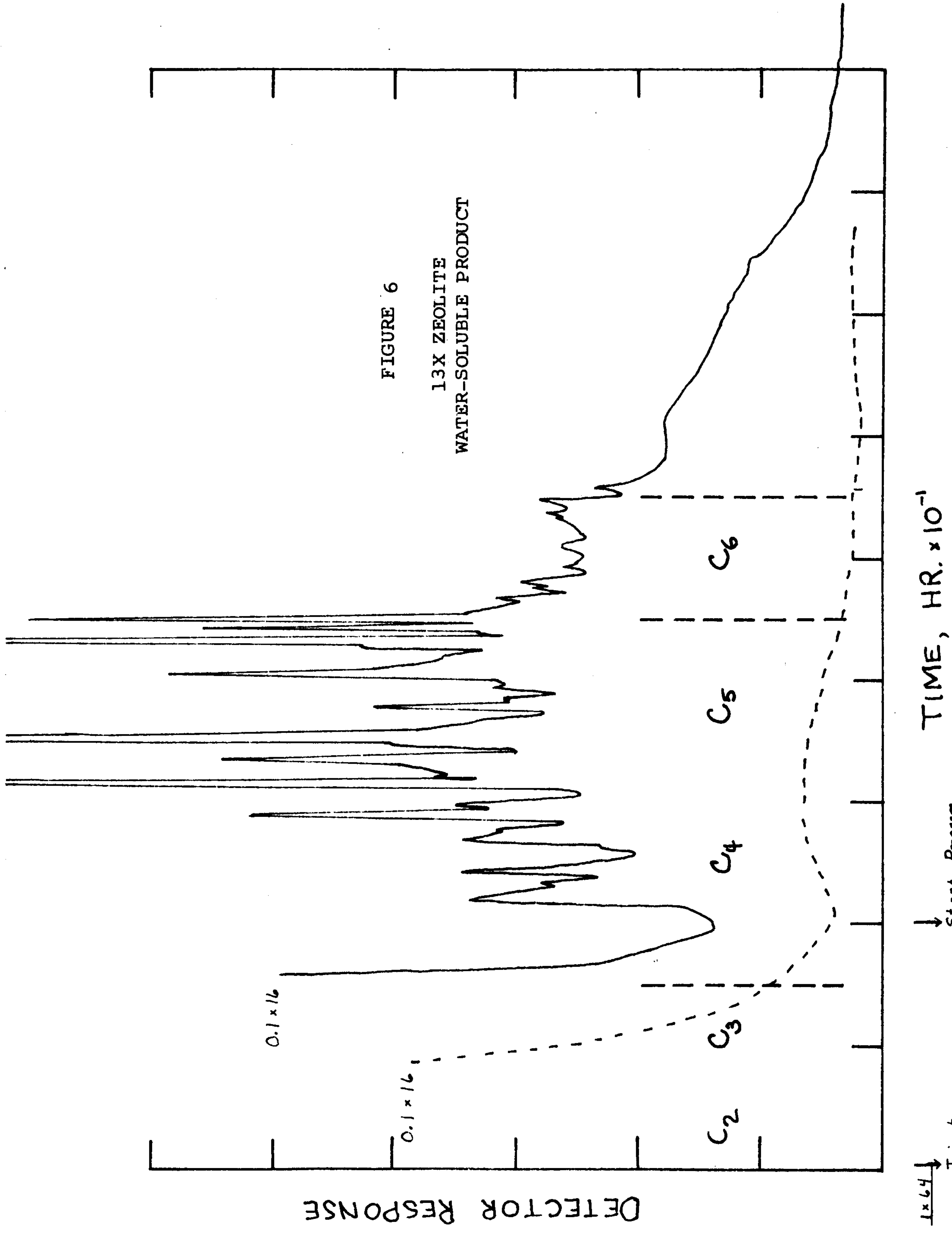


FIGURE 6

13X ZEOLITE
WATER-SOLUBLE PRODUCT

Table 4

ADSORPTION-IRRADIATION OF FORMALDEHYDE ON ZEOLON-H

	Para-Formaldehyde	Zeolon-H
Irradiation Dose rads x 10^7	0.89	1.7
Formaldehyde, adsorbed, %	--	16.0
Water-soluble Products, moles/ 100 moles of formaldehyde adsorbed	0.11	2.5
C4	0.02	0.00
C5	0.06	0.00
C6	0.01	0.08
Higher	0.02	2.42
	0.11	2.50
Conversion, moles/ 100 moles formaldehyde adsorbed		
C4	19	0
C5	52	0
C6	13	3
Higher	16	97
	100	100

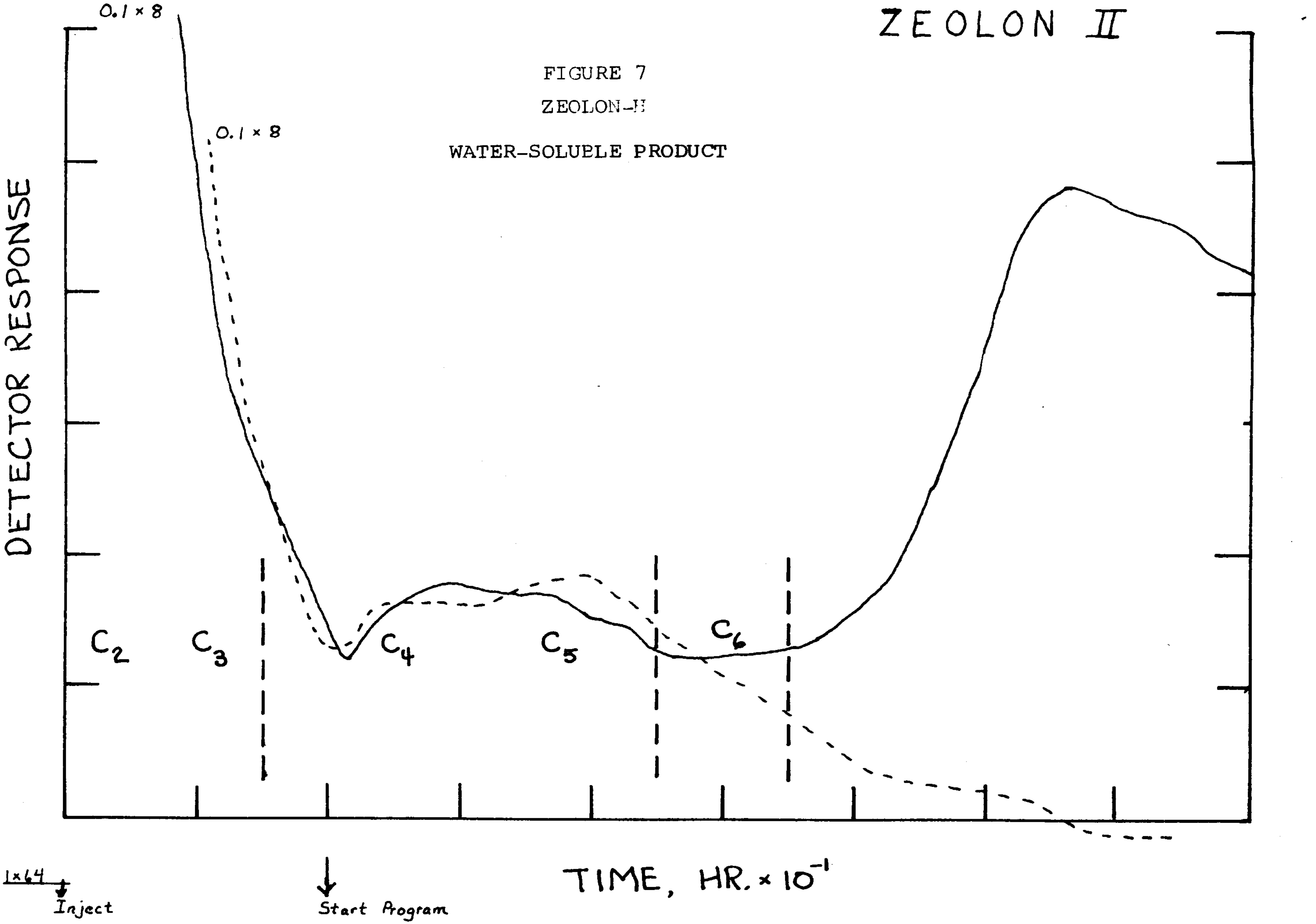


FIGURE 7
ZEOLON-H
WATER-SOLUBLE PRODUCT

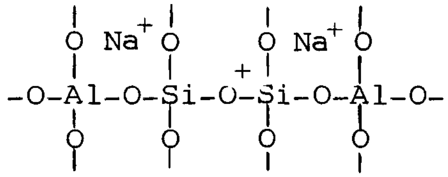
dimensions, but the formation of products higher than C-6 is striking (compare Figure 7 with Figure 6).

IV. DISCUSSION OF RESULTS

A. Free Radical Stabilization

The synthesis of monosaccharides by γ-irradiation of formaldehyde adsorbed on zeolite is, first of all, initiated by the generation of free radicals of undetermined form. The role of the zeolite in free radical stabilization can be clarified by the work of Stamires and Turkevich.[13]

With aluminum present in the four-coordinate state $(AlO_{4/2})^-$, γ-irradiation produces a paramagnetic defect in the zeolite which increases with increasing dose rate. This X_1 center signal is sensitive to oxygen and changes reversibly with temperature below 350°K according to the Curie-Weiss law. This finding indicates that the centers do not interact and exist in a homogeneous dispersion in the lattice of the aluminosilicate crystals. In a simplified planar representation of the defect, an electron hole is located between the O^{16} and Si^{24} atoms as follows:



$$-\mathrm{O}-\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{Al}}}-\mathrm{O}-\underset{\mathrm{O}}{\overset{\mathrm{O}\ (\mathrm{Na}^+)}{\mathrm{Si}}}-\overset{+}{\mathrm{O}}-\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{O}}{\overset{\mathrm{O}\ (\mathrm{Na}^+)}{\mathrm{Al}}}-\mathrm{O}-$$

Neither of the adjacent atoms has any nuclear magnetic moment. It is inferred that the displaced electron is delocalized and migrates over the entire aluminosilicate lattice.

With respect to 5A molecular sieve, it should be noted that the Si/Al ratio is ~~2~~1/1. Thus, the creation of suitable sites between two adjacent ($SiO_{4/2}$) is minimal compared with Type X and Zeolon zeolites. Also, considering the field gradient and electrostatic field in the ($SiO_{4/2}$) unit located next to the ($AlO_{4/2}$)-Na+ tetrahedron, it seems likely that γ-irradiation will produce less hole defects than would be present in a Type X sieve (Si/Al = ~~2.8~~1.4/1). This event was observed in the current study. Both 10X and 13X zeolites produced much greater quantities of water-soluble products than did the 5A zeolite.

The e.s.r. spectra of decationized zeolites was found to be appreciably different. In addition to the X_1-signal, a six-lined hyperfine structure was observed (X_2). This was assumed to be due to the interaction of a trapped electron with the nuclear moment of Al^{27}. This signal is associated with three-coordinated ($AlO_{3/2}$) sites and is not affected by oxygen. The extremely high ratio of Si/Al in Zeolon-H (~~10~~5/1) suggests the possibility of considerable three-coordination of aluminum and, therefore, the Zelon-H zeolite would have not only electron holes, but also trapped electrons from the γ-irradiation. The mechanism of reaction induced by the decationized zeolite, Zeolon-H, should be markedly different from that of either Type A or X zeolites. The data from the Zeolon-H experiment differed, both in magnitude of conversion and in product distribution.

B. Geometric Effects

The structure of Type A and X zeolites has been shown to consist of cuboctahedral cavities joined together in tetrahedral coordination.[14] The physical structure comprises series of channels interconnected through larger cavities. Each cavity has a free diameter of 11-12Å and is connected to four other similar cavities through tetahedrally-arranged access ports. These ports compose 12 silica and alumina tetrahedra which have an approximate diameter of either 4-5 or 8-9 Å (Type A or Type X zeolites, respectively). Further small cavities exist but these are not available except to small molecules. A cation is associated with every $(AlO_4)^-$ unit to give electrical neutrality. By exchange replacement of Na^+ with Ca^{++}, the access port sizes can be changed, as indicated in Table 1. The kinetic energy and elasticity of incoming molecules allows passage of molecules up to 0.5 Å larger than the free diameter of the aperture.

With Type A and X zeolites containing either alkaline or alkaline earth cations, the interaction of an adsorbed molecule with the lattice is weak and may be classified as van der Waals adsorption. Partial or complete removal of the cation can be effected by forming first the NH_4^+-form by ion exchange and then removal by outgassing at 500°C. Electron-accepting sites are produced which e.s.r. studies show are associated with $(AlO_{3/2})$ units.[15] These reach a maximum of 1.5×10^{19} spins/g in comparison with a maximum number of 2×10^{20} decationized sites/g. With the low ionization potential molecule, triphenylamine $(C_6H_5)N$, perturbation of the surface is much stronger and an electron change-transfer complex, $[(C_6H_5)_3N]^+ [(AlO_{3/2})]^-$, is formed; the free radical structure is stabilized due to the rigid electron-accepting sites of the crystal lattice. The maximum quantity of $(C_6H_5)N$ which can be adsorbed is limited by the effective volume of each molecule. Thus, one molecule per cavity is permitted (with perhaps some solvent). The maximum number of three-coordinated sites is one per large cavity, or 3×10^{20} sites/g ; this is only 20 times larger than that determined experimentally. Since the aluminosilicate structure is not altered, the above findings demonstrate that the pores are molecular in size with nearly a 1-to-1 correspondence of cavities and electron hole sites-produced by γ-irradiation.

Zeolon is a synthetic mordenite of rather recent development.[16] Studies comparable to that of A and X zeolites are not yet available. The mordenite structure[17] has the aluminosilicate framework, comprised of five-membered rings of tetrahedra with a free diameter of 6.6 Å; these provide a system of tunnel-like channels; interconnection by relatively small channels (2.8 Å free diameter) does not allow inter-channel access to most molecules. Because of the high Si/Al ratio, the content of $(AlO_{3/2})$ sites in the channels would be high. Thus, the ability to stabilize free radicals and electrons produced by γ-irradiation would be high. Zeolon-H is a decationized synthetic mordenite where the cation has been replaced by H^+, and the tunnel structure of approximately 10Å diameter extends for long distances in contrast to the interconnected cavity structure of A- and X-zeolites.

In related catalytic reactions, the use of the aluminosilicate channels for hydrogenation selectivity of large linolenic glyceride molecules was shown;[10] only the tail end of the long C-18 molecule was depicted as having access to catalytic sites within the zeolite channels. In a study of X-type molecular sieves for the alkylation of benzene by ethylene, the size of occluded large molecules was limited by the pore dimensions of the catalyst structure;[18] ethylene polymerization also produced large molecules limited in maximum size by the catalyst pore dimensions.

These studies suggest that monosaccharides synthesized within A- and X-zeolites will be limited in maximum size by the cavity dimensions of the open lattice structure, that free radical stabilization and synthesis will be highest with the X- and Zeolon-H zeolites and that the Zeolon-H zeolites dimensions will not limit appreciably the maximum possible molecular size of the synthetic monosaccharides.

C. Mechanism of Monosaccharide Synthesis

The initiation of synthesis is caused by γ-irradiation of formaldehyde to produce free radicals of undetermined structure. A limited degree of synthesis was possible when paraformaldehyde was γ-irradiated. After adsorption of formaldehyde upon zeolites, the free radicals are much more stable as demonstrated by the stability of the methyl radical.[7] This effect was demonstrated by the greater degree of synthesis (13-fold increase) with Type A zeolite due to free radical stabilization by electron-hole traps in the lattice. Similar experiments with Type X zeolites caused a further 10-fold increase in synthesis due to the greater amount of electron hole traps possible for free radical stabilization. The maximum size of the synthetic product was limited by the cavity dimension of 11-12 Å. This corresponds to a straight-chain monosaccharide of approximately 9-10 carbon atoms. The tailing of the gas chromatograms suggests that the maximum chain length is cut off at about this length.

The nature of the product distribution of monosaccharides is not readily inferred from the access pore diameter. In the case of the 5A zeolite, some importance might be attached to the 5 Å port as a factor in synthesis. However, the greater electron hole trapping capability of the larger-pored 10X and 13X zeolites does not allow this comparison. There is a slight difference in access ports of the 10X and 13X sieves (8 and 9 Å diameter); the similarity of conversions and product distribution suggests that this difference did not contribute appreciably to the synthesis mechanism. The calcium content of the 5A and 10X sieves has no apparent bearing on the product synthesis; this contrasts markedly to the reaction in aqueous solutions where calcium ion has a significant catalytic influence.

The mechanism of synthesis with decationized Zeolon-H is appreciably different from that of both the A- and X-molecular sieves. According to the proposed mechanism, not only can electron hole traps stabilize free radical formation but electrons themselves can exist in stable form on the $(AlO_{3/2})$ sites thereby prolonging free-radical synthesis. In addition, the matrix comprises essentially long channels, approximately 10 Å in diameter. Thus, there is no limitation on molecular size. Synthesis of C_6- and higher monosaccharides by irradiation of formaldehyde adsorbed on Zeolon-H zeolite is in agreement with this view. The low conversion suggests product decomposition during extended exposure of these relatively large molecules.

One aspect of the monosaccharide synthesis was not achieved--isolation of specific monosaccharide entities. Undoubtedly, γ-irradiation produces product distributions which are more random than those achieved by chemical syntheses. However, the products are water-soluble, reducible compounds which, upon silylation, convert to complex mixtures of compounds with volatilities similar to that of natural monosaccharides. If large amounts of irradiated product were available, identification of specific compounds would be possible.

V. CONTINUOUS SYNTHESIS OF SUGAR AND FUTURE RESEARCH

Obviously, it is impossible to discuss an operating system for sugar production on the basis of this feasibility study. However, it is possible to indicate that a process could be devised even with the preliminary information now available. Thus, catalyst beds containing 100 lbs of zeolite (2.27 cu. ft) would produce approximately 0.5 lbs of water-soluble product per day according to a scheme proposed in Table 5. The product as now prepared would not be suitable for human consumption. The crude product, at best, is only faintly sweet and requires considerable study for classification as edible. Divided into four beds containing 25 lbs of zeolite, a degree of continuity would be attained with batch processing.

Several directions for future research are suggested. First, it may be possible to decrease the irradiation dose of the process. It is possible that the experimental irradiations used are orders of magnitude higher than necessary. Second, with the aid of the mechanism proposed, it may be possible to select zeolites which will maximize monosaccharide synthesis for selected molecular ranges, e.g., for C-3, C-5 or C-6. This selectivity would be achieved by the pore dimensions and type of zeolite. Third, a logical extension of the proposed synthesis is to utilize hydrogen for chain stopping. In particular, selectivity for C-3 product and hydrogenation might produce glycerol in one step. Of the myriad of possible products, glycerol is edible and has none of the isomeric complications of larger molecules. Fourth, with the optimum zeolite and suitable irradiation conditions, it will be necessary to study the recovery of unreacted formaldehyde and conversion to byproducts. In the current study, neither unreacted formaldehyde

Table 5

CONTINUOUS PRODUCTION OF SUGAR-LIKE PRODUCTS

Step No.	Process	Nominal Time, hrs.
1	Activate zeolite at 500°C and high vacuum	16
2	Formaldehyde adsorption	2
3	γ-Irradiation	20
4	Product extraction	2
5	Solvent removal, zeolite drying at 110°C and vacuum	8
	Total cycle	48

nor low molecular weight byproducts were determined. Fifth, the possibility of zeolite regeneration and continuous processing should be considered.

VI. SUMMARY

A process has been demonstrated for the experimental conversion of formaldehyde into sugar-like products. The process comprises γ-irradiation of formaldehyde adsorbed on zeolites. In a single contact, the conversion of formaldehyde to water-soluble, reducible products is approximately 10%, but may be either higher or lower. Based on the present study and e.s.r. findings of others, a synthesis mechanism has been proposed. The γ-irradiation causes the formation of free radicals from formaldehyde; the zeolite acts to stabilize free radicals, both in initiation and in growing chains, by providing rigid electron traps; the chains continue to grow until termination by either a chain-stopping event or eventually by the physical dimensions of the zeolite cavity (11-12 Å for A and X zeolites); this sequence produces up to some 1000 times more product than in the absence of zeolite. With another zeolite with a tunnel-like matrix, the product distribution is radically different and much longer chains were possible.

BIBLIOGRAPHY

1. Butlerov, A., "Bildung einer Zuckerartigen Substanz durch Synthese," Ann., 120, 295-8 (1961).

2. Langenbeck, W., "Die Formaldehydkondensation als organische Autokatalyse", Naturwiss., 30, 3024 (1942).

3. Balezin, C. A., "Mechanism of the Formation of Sugars from Formaldehyde," J. Gen. Chem., USSR 17, 2288-91 (1947).

4. Ackerlof, G. C., and Mitchell, P.W.D., "A Study of the Feasibility of the Regeneration of Carbohydrates in a Closed Circuit Respiratory System," Final Technical Report, Contract No. NASr-88, NASA, Environmental Control Research Branch, Ames Research Center (FMC Corporation) (1963).

5. Shapira, Jacob., Private communication pertaining to research at Ames Research Center NASA (1967).

6. Gabel, N. W., and Ponnamperuma, C., "A Model for the Primordial Origin of Monosaccharides," Biochemica et Biophysica Acta, (1967).

7. Noble, G. A., Serway, R. A., O'Donnell, A., and Freeman, E. S., "Stability of Methyl Radicals Trapped in a Zeolite Matrix," J. Phys. Chem., 71, 4326-9 (1967).

8. Sutherland, J. W., Sethi, D., and Goodrich, R., "Radiolysis of Carbon Dioxide in the Adsorbed State," J. Phys. Chem., 71, 4422-9 (1967).

9. Weisz, P. B., and Frillette, V. J., "Intracrystalline and Molecular-Shape-Selective Catalysis by Zeolite Salts." J. Phys. Chem., 64, 382 (1960).

10. Riesz, C. H., and Weber, H. S., "Hydrogenation Catalysts prepared on Molecular Sieve Supports," J. Am. Oil Chemists' Soc., 41, 464-8 (1964).

11. Sweeley, C. C., Bentley, R., Makita, M., and Wells, M. W., "Gas-Liquid Chromatography of Trimethylsilyl Derivatives of Sugars and Related Substances," J. Am. Chem. Soc., 85, 2497-2507 (1963).

12. Parcher, P. F., and Urone, P., "An Improved Solution Coating Technique for Gas Chromatography Supports," J. Gas Chromatography, 2, 184-5 (1964).

13. Stamires, D. N., and Turkevich, J., "Paramagnetic Resonance Absorption of γ-Irradiated Synthetic Zeolites," J. Am. Chem. Soc., 86, 757-61 (1964).

14. Breck, D. W., Eversole, W. G., Milton, R. M., Reed, T. B., and Thomas, T. L., "Crystalline Zeolites," J. Am. Chem. Soc., 78, 5963-76 (1956).

15. Stamires, D. N. and Turkevich, J., "Electron Spin Resonance of Molecules Adsorbed on Synthetic Zeolites," J. Am. Chem. Soc., 86, 749-757 (1964).

16. Keough, A. H., and Sand, L. B., "A New Intracrystalline Catalyst," J. Am. Chem. Soc., 83, 3536 (1961).

17. Meier, W. M., "The Crystal Structure of Mordenite," Z. Kristallogr., 115, 439 (1961).

18. Venuto, P. B., and Hamilton, L. A., "Reverse Molecular Selectivity and Aging in a Zeolite-Catalyzed Alkylation," I & EC Research and Development, 6 190-2 (1967).

DISTRIBUTION LIST

Copy No.____

Copy No.	Recipient
1-2 + 1 Reproducible	NASA/Ames Research Center Moffett Field, California 94035 Attention: Patent Counsel
3-5	NASA/Ames Research Center Moffett Field, California 94035 Attention: Contract Officer Mark A. Greene
6	NASA/Ames Research Center Moffett Field, California 94035 Attention: Environmental Control Research Branch Dr. Jacob Shapira
7	IIT Research Institute Physical Chemistry Files
8	IIT Research Institute Editors, D. J. McPherson, M. J. Klein
9	IIT Research Institute G. E. Burkholder, Main Files
10	IIT Research Institute C. H. Riesz
11	IIT Research Institute Eli S. Freeman