v. 38, no. 8, Apr. 15, 1963 · p 1939-1944 [illegible]

Repr~~inted~~ from ~~The Journal of~~ Chem~~ical~~ Phys~~ics~~, ~~Vol~~. 38, No. 8, 1939–1944, 15 April 1963
Printed in U. S. A.

Shock-Tube Study of Carbon Dioxide Dissociation Rate

6 p

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(Received 13 December 1962)

N64 10290# code none

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The homogeneous dissociation rate of carbon dioxide, diluted with large amounts of argon, was measured in a shock tube by two independent methods: (a) by the single-pulse technique, in which the gas reacts behind a reflected shock, is quenched by a rarefaction wave, and is later analyzed chemically; and (b) by measurements of light intensity in the blue continuum due to $CO_2(^3\Pi) \rightarrow CO_2(^1\Sigma) + h\nu$. The results of the two experiments agree. The rate is given by $d[CO]/dt = k[CO_2][M]$, with $k = 3\times10^{11}T^{\frac{1}{2}}\exp(-86\,000/RT)$ cm^3 moles^{-1} sec^{-1}. Dissociation evidently does not proceed directly from ground-state CO_2 to ground-state CO and O. The mechanism probably involves the intermediate electronically excited state $CO_2(^3\Pi)$, the rate-controlling process being associated with its formation.

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INTRODUCTION

Many studies have been made in recent years of the high-temperature dissociation rates of simple molecules. This activity has been due chiefly to the availability of shock tubes as workable tools of research. The greater part of the effort has been devoted to homonuclear diatomic molecules; polyatomic molecules have received less intensive study, although the decomposition rates of several species have been measured.

A number of authors have suggested that high-temperature dissociation reactions proceed from a nonequilibrium population of upper vibrational levels (e.g., references 1–3). If so, the usual classical treatments should fail to explain the data. One of the consequences of such a failure is that the measured rate constants, when fitted to an Arrhenius equation, show an activation energy E less than the bond dissociation energy D. Most of the experimental data on high-temperature dissociation do, in fact, behave in this manner. Nevertheless, by invoking a treatment that includes contributions of internal degrees of freedom to the activation energy,[4] it has generally been possible to set the activation energy equal to D and to fit the data (e.g., references 5–7).

When this procedure is applied to the rate constants for the dissociation of the larger polyatomic molecules, it is not necessarily true that a successful fit of the data reveals the number of degrees of freedom contributing. So many degrees of freedom may legitimately be invoked that very large differences between D and E may be accommodated. Carbon dioxide, on the other hand, being linear and triatomic, is the simplest kind of polyatomic molecule. It was thought for this reason that its dissociation rate might profitably be studied.

This paper describes measurements of the rate of homogeneous thermal dissociation of carbon dioxide in a shock tube. The gas was diluted with large amounts of argon to improve shock-tube performance and to act as a constant-temperature bath. The mixtures were very carefully dried. The rate was measured by two independent methods: (a) by the single-pulse technique of Glick, Squire, and Hertzberg[8]; and (b) by measurements of light intensity in the blue continuum, the emission that is characteristic of carbon monoxide-containing flames.

APPARATUS AND PROCEDURE

Shock Tube

The shock tube was of the single-pulse type and was similar to that described by Glick, Squire, and Hertzberg.[8] It was made up of sections of $2\frac{1}{2}$-in.-i.d. stainless steel tubing so that the ratio of reactor to driver length could be changed. The reactor had a maximum length of 101 in., the driver 56 in. The dump-tank volume was 800 cu ft. Metal diaphragms, separating the driver from the reactor and from the dump tank, were ruptured by plungers; these were actuated by shock waves generated in an auxiliary tube.

The basic instrumentation consisted of four miniature piezoelectric pressure transducers. Three of them, located 25.0, 12.6, and 2.6 in. from the end plate, operated the start–stop circuits of 2-μsec time-interval meters so as to give two velocity measurements for each wave. The fourth transducer was a calibrated SLM (Kistler Instrument Corporation) pickup mounted in the end plate. Its output, recorded on an oscilloscope, gave the pressure–time history in the reaction zone behind the reflected shock.

Since the aim was to study the dry reaction, care was

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[1] E. E. Nikitin and N. D. Sokolov, J. Chem. Phys. **31**, 1371 (1959).

[2] H. O. Pritchard, J. Phys. Chem. **65**, 504 (1961).

[3] B. Widom, 139th Meeting, American Chemical Society Paper No. 3, Division of Physical Chemistry (March 1961).

[4] L. S. Kassel, *The Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Company Inc., New York, 1932).

[5] H. B. Palmer and D. F. Hornig, J. Chem. Phys. **26**, 98 (1957).

[6] M. Camac and A. Vaughan, J. Chem. Phys. **34**, 460 (1961).

[7] W. Tsang, S. H. Bauer, and M. Cowperthwaite, J. Chem. Phys. **36**, 1768 (1962).

[8] H. S. Glick, W. Squire, and A. Hertzberg, Symp. Combust. 5th Pittsburgh, **1954**, 393 (1955).

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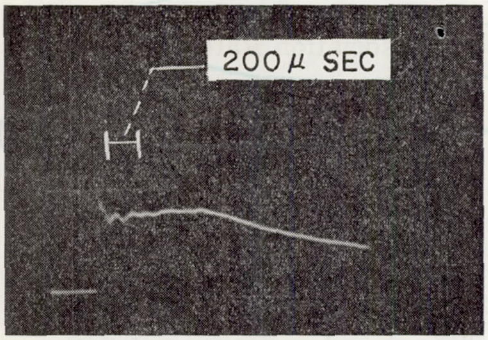

FIG. 1. Typical pressure trace.

taken to exclude atmospheric or other sources of water vapor. The tube was always pumped down to about 4 μ of mercury before filling, and had a leak rate of 1 to 2 μ/min. The tube was isolated from the pump by a cold trap cooled in liquid nitrogen.

Gas Mixtures

Carbon dioxide–argon mixtures were prepared by the method of partial pressures. At the partial pressures of carbon dioxide used, deviations from ideal-gas behavior were negligible. Mixtures were prepared and stored in stainless steel tanks which had been evacuated for several hours, and were allowed to stand for several days before samples were withdrawn. Gas-chromatographic analysis assured that the expected composition was attained, i.e., that mixing was complete.

The argon used had a stated purity of 99.999+%, and was cold-trapped before admission to the storage vessel as a further precaution against admission of water. Dry ice was a convenient source of carbon dioxide. It was purified by subliming about three-quarters of a sample, placed in a vacuum system, into a trap at -196°C. Of this trapped fraction about one-quarter was pumped off and the middle one-half used to prepare the mixture.

Gas Analysis

Samples of gas that had been heated by the reflected shock and quenched by the rarefaction wave were withdrawn within 30 sec after each run through a small valve in the endplate. Analysis was made by means of a gas chromatograph, modified so that carbon monoxide and carbon dioxide could be analyzed with helium carrier gas in the presence of excess argon. Peak areas were planimetered and compared with those obtained in calibration runs with known mixtures. The error in measured carbon monoxide concentration was $\pm 3\%$, and in carbon dioxide concentration, $\pm 2\%$.

Optical Equipment

In order to study the light emitted from shock-heated mixtures, it was necessary to modify the shock tube. A small calcium fluoride window was installed, and a new mounting for the SLM pressure transducer was provided at the same axial position as the window. A new endplate, with a plug machined to slip-fit into the tube, moved the back wall to a plane 1 in. downstream of the plane in which the window and pressure pickup were situated.

Complete spectra of the emitted light were obtained with a small quartz spectrograph. Time-resolved emission intensity at 3510 Å was measured by means of a grating monochromator and photomultiplier tube. With 0.50-mm entrance and exit slits, the monochromator had a bandpass of 33 Å.

RESULTS

Gas-Analysis Experiments

In each experiment, the following data were obtained: incident shock velocity (over two intervals); pressure–time history in the reaction zone; initial temperature and pressure; and analysis of the reacted and quenched gas sample.

From the two velocity measurements, the velocity of the shock at the back wall was determined by linear extrapolation. The pressure and temperature at which the reaction was assumed to proceed were calculated by the reflected-shock method of Markstein.[9] For these calculations, full thermal equilibrium was assumed, but the chemical composition was assumed to remain constant during the reaction.

Figure 1 shows a typical pressure trace. The flat-topped character was achieved by tailoring the driver-gas composition to eliminate interaction between the reflected shock and the contact surface.[10] It may also be seen that there is little indication of a gradual compression of the gas behind the reflected shock, due to the pressure gradient created by attenuation of the incident shock.[11] Many of the traces did show a pressure rise, but it was always very slight.

The assumption of constant reaction conditions may now be discussed in more detail. The dissociation would normally be expected to lower the temperature as it progressed, and, for the runs in which the conversion of CO_2 amounted to a twentieth or more of the quantity originally present, the drop would be significant for this experiment. However, the gradual compression of the reacting gas tends to increase the temperature. If this compression is considered to be adiabatic, the expected temperature rises are comparable to the expected temperature drops due to dissociation. To the extent that these opposing effects counteract one another, reaction conditions will remain essentially constant. As is seen shortly, the data themselves provide added evidence that conditions did not change appreciably with time.

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[9] G. H. Markstein, ARS J. **29,** 588 (1959).

[10] H. B. Palmer and B. E. Knox, ARS J. **31,** 826 (1961).

[11] G. Rudinger, Phys. Fluids **4,** 1463 (1961).

In addition to providing assurance of constant reaction conditions, the pressure traces also showed the reaction time. This was taken as the time from shock reflection to arrival of the rarefaction wave at the end plate. Measurement of reaction time was somewhat subjective, so it was carried out independently by two persons, and the results averaged. Reaction times shorter than about 80 μsec could not be read from the oscilloscope traces because of confusion from the ringing of the pressure-transducer signal (Fig. 1). The uncertainty in reaction time is estimated at about 10% for the shortest times (less for longer times). Its effect was reduced, however, by plotting values of [CO] against time for conditions of nearly the same temperature, pressure, and initial concentration and determining the rate from a line drawn through the points and passing through the origin. The spread in temperature for any given group was at most ±10°C.

Figure 2 shows least-square plots of [CO] against time for three such groups of data. There was in general a linear increase in [CO] with time, so that $d[\mathrm{CO}]/dt$ was easily determined as the slope of the line. Only two of the sets of data plotted as curves; the curvature may have been caused by falling temperature, as discussed above, and may also have been influenced by back reaction. However, even in these two cases, the initial rate could be determined graphically with reasonable confidence from the initial slope of the curve. It should be noted that the data obtained for the 3.44% mixture at the highest temperature used in the gas-analysis experiments, 2860°K, were probably subject in some measure to this effect. The rate was therefore expected to be somewhat low. However, it fits in with data obtained at higher temperatures by means of light-emission measurements, and was therefore retained.

The order of the reaction with respect to initial carbon dioxide concentration, $[\mathrm{CO_2}]_0$, was determined by comparison of data at essentially the same temperature and pressure, but with different initial concentrations. The reaction was found to be first order in $[\mathrm{CO_2}]_0$. Comparison of data (Fig. 3) for different pressures showed that the over-all order is about two. Therefore, rate constants were calculated from the expression

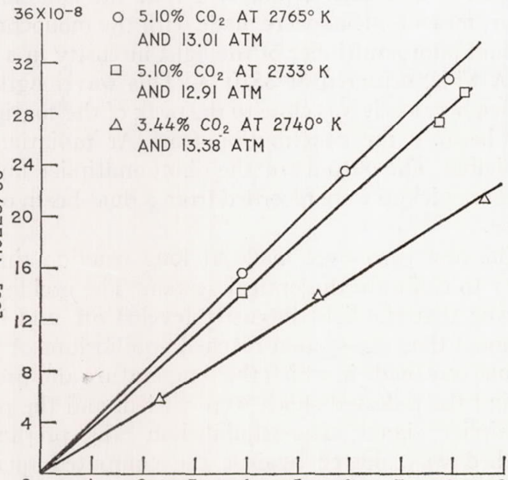

FIG. 2. Concentration of CO vs time.

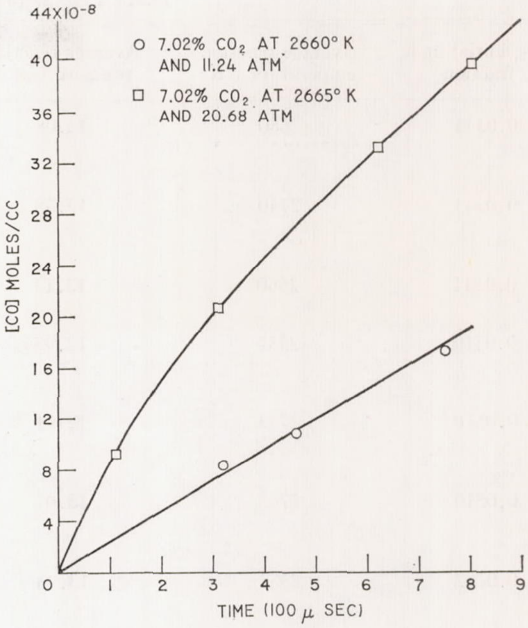

FIG. 3. Pressure dependence of reaction rate.

$$d[\mathrm{CO}]/dt = k[\mathrm{CO_2}]_0[M], \qquad (1)$$

where $d[\mathrm{CO}]/dt$ is the rate at zero time. The results are listed in Table I.

Figure 4 is an Arrhenius plot of the dissociation rate constants. A least-squares fit gives

$$k = 3\times10^{11}T^{\frac{1}{2}}\exp(-86000/RT)\,\mathrm{cm^3\ moles^{-1}\ sec^{-1}}. \qquad (2)$$

Light-Emission Experiments

Kaskan found in work with flames[12] that the intensity of light, in a narrow spectral region of the characteristic blue emission from flames, is proportional to the product of concentrations $[\mathrm{CO}(^1\Sigma)][\mathrm{O}(^3P)]$. White later found that this also holds true in the case of detonation waves[13]; his observations were made at three different wavelengths. It was decided to attempt to make use of these observations for an independent determination of the rate constant.

Preliminary to this, spectrograms were taken of the radiation from shock-heated argon and argon–carbon dioxide mixtures. Figure 5 shows densitometer traces of spectrograms obtained with Ar and with Ar–$\mathrm{CO_2}$ mixture. Fairbairn and Gaydon[14] did not observe the

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[12] W. E. Kaskan, Combust. Flame **3**, 39 (1959).

[13] D. R. White, Phys. Fluids **4**, 465 (1961).

[14] A. R. Fairbairn and A. G. Gaydon, Nature **175**, 253 (1955).

TABLE I. Experimental data and rate constants.

CO_2, initial mole fraction	Average reaction temperature (°K)	Average reaction pressure (atm)	Reaction time (μsec)	CO, mole fraction in reacted gas	Bimolecular rate constant
0.0344	2680	13.08	80	0.00031	
			240	0.00069	
			880	0.00311	1.66×10^6
0.0344	2740	13.38	230	0.00099	
			540	0.00235	
			860	0.00359	2.079×10^6
0.0344	2860	13.13	220	0.00221	
			230	0.00217	5.056×10^6
0.0510	2557	12.95	380	0.00098	
			810	0.00216	
			940	0.00217	0.792×10^6
0.0510	2733	12.91	390	0.00244	
			770	0.00478	
			820	0.00521	2.138×10^6
0.0510	2765	13.01	390	0.00275	
			590	0.00409	
			790	0.00537	2.360×10^6
0.0702	2552	13.93	225	0.00057	
			885	0.00308	
			920	0.00330	0.737×10^6
0.0702	2601	14.11	260	0.00105	
			530	0.00227	
			830	0.00358	
			910	0.00352	0.883×10^6
0.0702	2660	20.68	110	0.00098	
			310	0.00220	
			620	0.00352	
			800	0.00417	1.241×10^6
0.0702	2665	11.24	320	0.00165	
			460	0.00210	
			750	0.00339	1.292×10^6
0.0702	2771	14.19	290	0.00358	
			365	0.00413	
			535	0.00546	
			770	0.00635	3.059×10^6

blue CO flame radiation in shock-tube experiments with Ar–CO_2 mixtures, and concluded that the emission was not due to thermal excitation of CO_2. This conclusion is consistent with our work, since the characteristic blue continuum was recorded only when, on the basis of the gas-analysis experiments, an appreciable amount of CO_2 was expected to dissociate to CO and O. We also observed, as they did, that the intensity of Ar radiation is much reduced by the presence of CO_2; this may readily be seen by comparison of Figs. 5(a) and 5(b). The spectra from Ar–CO_2 mixtures did not show any positive evidence of banded structure. It is possible that the spectral resolution was too low to reveal it; however, Gaydon[15] implies that at high temperatures and pressures such as were used in our work the process leading to continuum radiation will be the predominant one.

After it had been established that the emission did occur, measurements were made with the monochromator and photomultiplier of the light intensity in a band 33 Å wide, centered at 3510 Å. This wavelength was chosen because it was close to the peak of the continuum and because the contribution from Ar radiation was negligible. The outputs of the photomultiplier and the pressure pickup were recorded from a dual-beam oscilloscope.

The first runs were made at long reaction times in order to calibrate the optical system. The oscillograms showed that the light intensity leveled off, and it was assumed that the system reached equilibrium. A series of runs was made in which the temperature and pressure behind the reflected shock were varied, and the photomultiplier signal after equilibrium was presumably reached was plotted against the computed quantity ([CO][O]) computed for equilibrium. The result was a straight line through the origin, as expected on the basis of Kaskan's work.[12] Thus, an empirical calibration

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[15] A. G. Gaydon, *The Spectroscopy of Flames* (John Wiley & Sons, Inc., New York, 1957), Chap. VI.

constant, A, was obtained for the optical system used from the least-squares slope of the line.

If it is supposed that the same constant holds when complete equilibrium does not exist, $d[\mathrm{CO}]/dt$ may be obtained from the intensity–time traces. In the very early stages of the dissociation of CO_2, the concentrations of CO and of O will be essentially equal. Consequently,

$$[\mathrm{CO}][\mathrm{O}]\cong[\mathrm{CO}]^2=I/A, \tag{3}$$

where I is the signal measured from the trace at any given early time. The initial slope of a plot of $(I/A)^{\frac12}$ vs time is therefore equal to the initial rate $d[\mathrm{CO}]/dt$.

This technique was applied to several runs with 7.02% mixture and, using Eq. (1), values of k were calculated. These rate constants are plotted in Fig. 4 as filled square symbols. The line is the least-squares line through the gas-analysis data. It is seen that there is excellent agreement between the two sets of k's. Moreover, the light-emission data extend the experiment to a higher range of temperatures, where the gas-analysis method failed because reaction times could not be made short enough to obtain data on the initial rate.

DISCUSSION

The apparent activation energy of 86 kcal is much less than the 126.7 kcal required to dissociate ground-state CO_2 to ground-state products. Therefore, either the Arrhenius expression is inadequate, or the rate measured is not that of the direct ground-state to ground-state reaction.

It has repeatedly been found that high-temperature dissociation rates show an Arrhenius activation energy that is much less than the bond dissociation energy, D. This occurs with both diatomic and simple polyatomic molecules. In many instances, the data have been rationalized by means of a treatment in which account is taken of energy stored in internal degrees of freedom,[4] by an additional term of the form $(D/RT)^{S-1}/(S-1)!$ Here, S represents one-half the number of classical squared terms contributing.

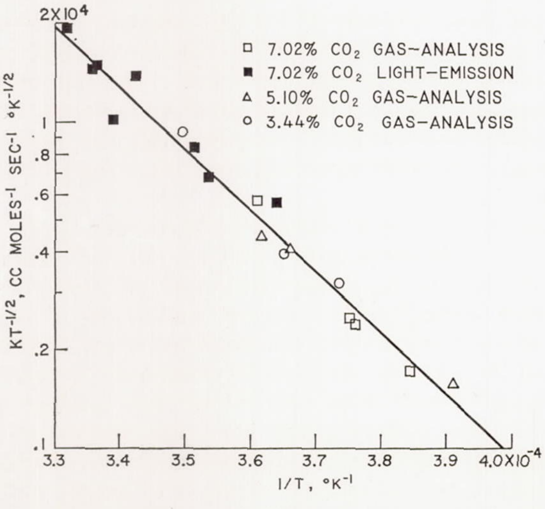

FIG. 4. Arrhenius plot of dissociation rate constants.

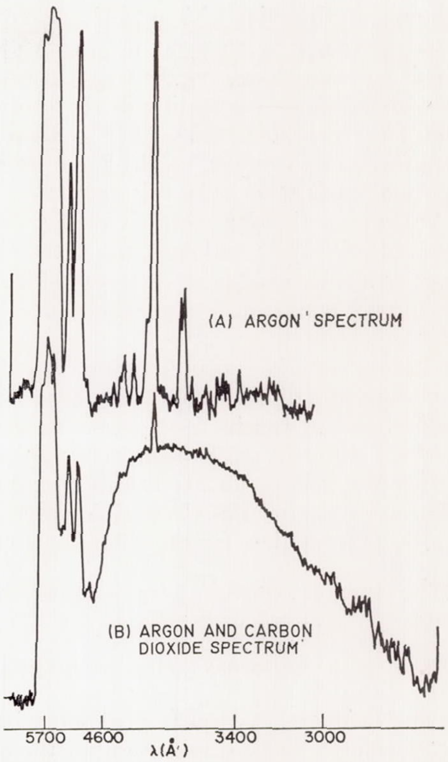

FIG. 5. Densitometer traces of shock-tube emission spectrograms.

A least-squares fit of the present data to such an expression, with $D=126.7$ kcal, is given by the following equation:

$$k=7.38\times10^5T^{\frac12}\frac{(D/RT)^{7.11}}{(7.11)!}\exp\left(\frac{-D}{RT}\right)\mathrm{cm}^3\ \mathrm{moles}^{-1}\ \mathrm{sec}^{-1}. \tag{4}$$

The exponent $(S-1)=7.11$ corresponds to about 16 classical squared terms. In a CO_2–Ar collision, there could be eight for vibrations, two for rotations, and one for the translation of each species along the line of approaching centers, for a total of 12. Thus, the requirement that S be about 16 is physically unreasonable.

Another possible explanation for a low Arrhenius activation energy is that the state from which dissociation occurs may not have an equilibrium population. Although a number of authors have discussed this problem, only Nikitin and Sokolov[1] offer readily-applied equations with which to calculate dissociation rates of polyatomic molecules. When their expressions were used to calculate CO_2 dissociation rate constants, the results were about one order of magnitude higher than the measured values. This is perhaps not too bad. However, when calculated k's were plotted in the Arrhenius fashion, that is, as $\ln(kT^{-\frac12})$ against $1/T$, they fell on a straight line with an activation energy of 112 kcal, compared to 86 kcal for the experimental data. This prompted us, incidentally, to re-examine Nikitin and Sokolov's calculation of the bromine dissociation rate constant, which they compared with Palmer and Hornig's values,[5] and offered as evidence in support of their theory. In this case, too, the predicted Arrhenius activation energy is much greater than the observed one. Thus, although the theory can predict more or less reasonable rate constants, it does not show the proper temperature dependence for either CO_2 or Br_2.

Since it does not seem possible to force the data into the framework of a direct ground-state to ground-state dissociation, one alternative is to accept the Arrhenius fit and seek a different mechanism. It is proposed that dissociation proceeds via an electronically excited state, $CO^2(^3\Pi)$, and that the rate-determining step is associated with its formation, for the following reasons:

(1) The reaction responsible for the blue continuum is probably[15]

$$CO(^1\Sigma)+O(^3P)\rightarrow CO_2(^3\Pi)\rightarrow CO_2(^1\Sigma)+h\nu.$$

Griffing and Laidler[16] have constructed potential-energy surfaces showing it to be reasonable that the observed energy range of the emitted light, 55 to 95 kcal, corresponds to the above process, with the CO_2 $(^1\Sigma)$ in a vibrationally excited state. The observed activation energy, 86 kcal, falls nicely into this range.

(2) The rate constants from the light-emission experiments were based on the assumption that the calibration constant, determined at equilibrium, also holds during the approach to equilibrium. The agreement between the light-emission and gas-analysis results supports this assumption. Therefore, equilibrium exists among $CO(^1\Sigma)$, $O(^3P)$, and $CO_2(^3\Pi)$ during the dissociation. This in turn implies that the rate-controlling step precedes the light-emitting reaction.

(3) The direct reaction involves a change in multiplicity and hence is "forbidden."

There are two ways in which the reaction $CO_2(^1\Sigma)\rightarrow CO_2(^3\Pi)$ might occur. First, it could be a collision-induced transition from the vibrationally excited singlet state. Second, it could be caused by a collision of the second kind between CO_2 and a suitably excited triplet Ar atom; in this event, the activation energy would correspond to vibrational excitation of the singlet CO_2, because little or no activation energy would be required for the electronic transition. The second possibility is attractive, because it would account for the marked reduction in the intensity of Ar radiation when CO_2 is present.

It is not possible at present to choose between the alternatives. More experimental work, especially with diluent gases other than Ar, might throw added light on the subject.

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[16] V. Griffing and K. J. Laidler, Symp. Combust. 3rd Madison, Wisconsin, **1948**, 432 (1949).