

manometric and the spectrophotometric data were subjected separately to a least squares treatment, giving the following equations for the temperature dependence

$$\log_{10} K_{p, \text{ atm}} = -\frac{2597.06}{T} + 7.83262 \text{ (manometric data)}$$

$$\log_{10} K_{p, \text{ atm}} = -\frac{2816.10}{T} + 8.41011 \text{ (spectrophotometric data)}$$

Thermodynamic data were calculated at 298.16°K. by extrapolating the temperature dependence equations for the equilibrium 30° below the temperature range of the measurements. At 298.16°K.

$$\log_{10} K_{p, \text{ atm}} = -0.87767 \text{ (manometric)}$$

$$\log_{10} K_{p, \text{ atm}} = -1.03482 \text{ (spectrophotometric)}$$

From

$$\Delta F = -RT 2.303 \log K_{p, \text{ atm}}$$

$$\Delta F = -1200 \text{ cal./mole (manometric)}$$

$$\Delta F = -1400 \text{ cal./mole (spectrophotometric)}$$

The standard error of $\log K_{p, \text{ atm}}$ for the manometric data was ± 0.0575 , while that for the spectrophotometric data was ± 0.129 . The corresponding standard errors for ΔF were therefore ± 78 and ± 176 cal./mole.

$$\Delta F = -1200 \pm 80 \text{ cal./mole (manometric)}$$

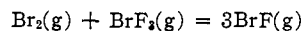
$$\Delta F = -1400 \pm 180 \text{ cal./mole (spectrophotometric)}$$

From the slopes of the least squares lines and their standard deviations, the enthalpy change accompanying the reaction was

$$\Delta H = 11,900 \pm 500 \text{ cal./mole (manometric)}$$

$$\Delta H = 12,900 \pm 700 \text{ cal./mole (spectrophotometric)}$$

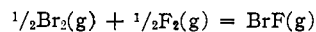
Using the more accurate manometric data, and taking the gases at 1 atm. and 298.16°K. as the standard state, the results may be summarized as



$$\Delta H^\circ = 11.9 \pm 0.5 \text{ kcal./mole}$$

$$\Delta F^\circ = -1.2 \pm 0.08 \text{ kcal./mole}$$

From these data it was possible to calculate the enthalpy and free energy of formation of bromine trifluoride, quantities which were not available previously. Thermodynamic data were available in the literature¹¹ for the reaction

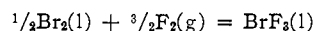


$$\Delta H^\circ_{298.16} = -18.4 \pm 0.5 \text{ kcal./mole}$$

$$\Delta F^\circ_{298.16} = -18.7 \text{ kcal./mole}$$

The standard state chosen for this calculation was the ideal gases at 1 atm. The values, obtained from spectroscopic data on the dissociation of bromine monofluoride,⁶ were based on the assumption that the fluorine was in the excited state and the bromine was not.¹¹

Using the more conventional standard states, the standard enthalpy and free energy of formation of bromine trifluoride were calculated for 1 atm. pressure and 298.16°K. The vapor pressure and enthalpy of vaporization of bromine trifluoride were obtained from the data of Oliver and Grisard.¹²



$$\Delta H^\circ_{\text{BrF}_3} = -75 \text{ kcal./mole}$$

$$\Delta F^\circ_{\text{BrF}_3} = -57 \text{ kcal./mole}$$

Acknowledgment.—The authors wish to express their appreciation to Mr. G. W. Redding for his assistance with the experimental determinations and to Professors Scott Wood and George Cady for their interest in the work.

(11) W. H. Evans, T. R. Munson and D. D. Wagman, *J. Research Natl. Bur. Standards*, **65**, 147 (1955).

(12) G. D. Oliver and J. W. Grisard, *This Journal*, **74**, 2705 (1952).

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Decomposition of Carbon Dioxide in a Radiofrequency Arc¹

BY KENNETH A. WILDE, BRUNO J. ZWOLINSKI AND RANSOM B. PARLIN

RECEIVED OCTOBER 8, 1956

A kinetic study has been made of the chemical processes that govern the decomposition of gaseous carbon dioxide in a 3 Mc. electric discharge in a flow system. Factorial experiments showed the following parameters to be of prime importance in controlling the decomposition into CO and O₂: pressure, flow rate and current. An analysis based on available thermodynamic, kinetic and spectroscopic information indicated the likely elementary chemical steps and experimental results were compared with theory through a simple hydrodynamic model. This kinetic scheme requires the reverse reaction between CO and oxygen atoms as well as the recombination of oxygen atoms as a terminating step. The former reaction explains the inertness of CO₂ in static radiation systems. The experimental flow rate dependence can be explained within experimental error and a semiquantitative interpretation of pressure and current effects is given.

Introduction

During the past few years, a series of investigations have been carried out by the senior authors on the chemical effects in gaseous radio frequency electric discharges which included studies on fixation of nitrogen,² formation of hydrazine,³ and irra-

diation of CO₂-H₂O mixtures.⁴ In the work reported herein, the decomposition of carbon dioxide was selected as a representative and a sufficiently simple chemical system whose study could serve as a model for a deeper understanding of the controlling physical and chemical processes in electric discharges with respect to more complex molecular systems.

A radiofrequency discharge in the range of approximately 3 megacycles was used. A flow apparatus was selected to facilitate chemical analysis

(1) Supported by the U. S. Atomic Energy Commission, Contract AT(11-1)-82. Presented at the A.C.S. Fall Meeting, Chicago, Ill., Sept. 1953. Abstracted from thesis of K. A. Wilde, submitted to the Faculty of the University of Utah in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Wm. S. Partridge, R. B. Parlin and B. J. Zwolinski, *Ind. Eng. Chem.*, **46**, 1468 (1954).

(3) W. H. Andersen, Ph.D. thesis, University of Utah, 1952.

(4) K. A. Wilde, B. J. Zwolinski and R. B. Parlin, *Science*, **118**, 43 (1953).

and to restrict the chemical effects to reactions initiated by the products of the primary action of the discharge. In the interpretation of the data the usual steady-state treatment of complex kinetic systems will be employed together with a simple hydrodynamical model to compare the results with experiment.

A considerable amount of work has been done on carbon dioxide decomposition in electric discharges; of the 12 studies reviewed,⁵⁻¹⁵ 11 were carried out in static systems, and only one in a flow system.¹⁶ Most of this work was exploratory in nature and little in the way of interpretation seems to have been attempted. In addition, the experimental conditions varied widely from those reported herein.

Experimental

Equipment and Procedure.—A conventional Pyrex glass flow system was employed. The carbon dioxide bled into the system analyzed to a minimum of 99.3% CO₂, the remainder approximating the composition of air. The analysis was based on two methods: (1) standard absorption methods in an Orsat apparatus and (2) absorption of CO₂ sample in standard KOH and back-titration of the excess base with standard HCl. Two traps in the feed gas line filled with concentrated sulfuric acid and anhydrous CaSO₄, respectively, reduced the water content of the feed gas to less than 0.001% by volume. A capillary manometric flow meter permitted observation of flow rates in the range of 0.4 to 100 cc./sec. (S.T.P.). From the flow meter the feed gas was directed through a spherical discharge tube (58 cc.) at right angles to the electrodes forming the high frequency arc. The conical nickel electrodes (solid angle of 18°) were mounted on Ni-plated screws to allow variation of electrode gap distance. The gap distance was measured with a cathetometer to an accuracy of about 0.1 mm. All studies were made with the discharge tube at ambient room temperatures. No direct measurement of arc temperatures were attempted; however, wall temperatures of 100 to 150° indicate that arc temperatures of 400 to 500° are very likely.

Power to the discharge tube was supplied by a U. S. Army aircraft transmitter, Type BC 375-E with a rated output of 150 watts. Radiofrequency power was measured in the conventional way with an assumed power factor of unity.^{2,3}

Analysis of Products.—The following decomposition species of CO₂ were assumed: CO, O₂, O₃, C₃O₂, and C(s). Carbon suboxide and solid carbon have not, in general, been observed in electric discharges in pure CO₂,^{7,13,15} and were not found in the present work. Solid carbon was not observed visually, neither was carbon suboxide detected in the Dry Ice trap. Traces of ozone were detected in conformity with most other investigations, where either no ozone or only traces thereof were found.^{7,8,13} Spreter and Briner¹⁵ found that only 0.5% of the total oxygen in the decomposition products was present as O₃. In the present work the silver foil test¹⁷ showed traces of ozone to be present in the gas immediately downstream from the arc, but not when the product gases were tested with KI solution several feet from the arc source. Either the ozone had only a transient sta-

bility or the silver foil was blackened by some other species, possibly atomic oxygen.

The exit gases were analyzed by the usual absorption methods for CO₂, CO and O₂ in a conventional Orsat apparatus and found to consist of these three gases plus a small quantity of N₂ from the feed gas. The infrared studies of the product gases on a Perkin-Elmer Model 12C spectrophotometer gave no indication of other products. It was concluded that, within the limits of the analysis (ca. 0.5%), the main stoichiometric chemical change occurring was the decomposition of CO₂ to CO and O₂. Since separate analyses for the three gases gave substantially the same result for the fractional decomposition, in the interest of ease and speed of analysis, only CO₂ was determined directly.

Precision.—The experimental error was determined for the following conditions: flow rate, 2.0 cc./sec. (S.T.P.), pressure, 70 mm., current, 115 ma., gap distance, 6.1 mm. and frequency, 3.0 Mc. The mean of five consecutive runs for the per cent. decomposition was 5.7% with a standard deviation of 0.23%. In each case the specific variable value used represented a median value for the experimentally available range and the error should not be appreciably different for other conditions.

Experimental Findings.—In order to investigate in a preliminary manner the numerous experimental parameters with a minimum number of runs, a 2⁶ factorial experiment was carried out and a variance analysis made. That is, six variables were investigated, each at two levels of their respective ranges. Statistical methods such as factorial experiments and variance analysis¹⁸ can be used to determine the presence or absence of a given experimental effect or, more precisely, whether the effect is statistically significant. These methods, in their present state of development, cannot give any information as to the exact nature of, or relationship among, the experimental effects.

The following six parameters were studied, each at two levels: pressure, flow rate, current, gap distance, surface (runs with and without glass wool packed in the discharge tube), and flow direction (gas stream parallel or perpendicular to the arc). On the basis of this factorial experiment the effect of flow direction was found to be small and was not pursued further. Since the arc plasma usually takes the form of a cylinder of diameter approximately half its height, this result would seem to indicate that the volume of the arc plasma is more important in determining yields than the linear dimensions. All the remaining parameters were found either to cause major effects or to influence the effects of other variables ("interactions"), and consequently were studied in detail. Yields (in terms of mole per cent. decomposition or fractional conversion) decreased more or less exponentially with increasing flow rate, but increased linearly with increasing current. Yields decreased slightly with increasing pressure, but were virtually independent of gap distance (range, 1 to 12 mm.), surface and frequency (range, 1.5 to 6.5 Mc). At the present time the only effects which can be given a theoretical interpretation are the ones represented by the data for varying flow rate at different currents and pressures, shown in Figs. 1 and 2 as x , fractional conversion, versus $1/F$, reciprocal mass flow rate. Further discussion of the experimental findings will be postponed until an analysis of the elementary steps responsible for the chemical action can be given in the next section together with a consideration of possible mechanisms for the decomposition of carbon dioxide.

A summary of the experimental conditions with ranges of values investigated for the pertinent variables are given in Table I. For purposes of comparison with other studies on the decomposition of carbon dioxide the energy yields obtained were of the order of 0.4 to 5.6 g./kilowatt-hour or 0.24 to 3.4×10^{-3} molecules decomposed per electron-volt, i.e., G values of 0.024 to 0.34.

Elementary Chemical Processes

In this section, a preliminary evaluation of the relative importance of certain elementary steps in the decomposition of CO₂ is given. Wherever possible the role of primary and secondary processes will be assessed in relation to the particular conditions and characteristics of electric discharges.

(18) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951.

- (5) J. N. Collic, *J. Chem. Soc.*, **79**, 1063 (1901).
 (6) W. Lob, *Z. Elektrochem.*, **12**, 282 (1906).
 (7) A. Holt, *J. Chem. Soc.*, **95**, 30 (1909).
 (8) A. Moser and N. Isgarischew, *Z. Elektrochem.*, **16**, 613 (1910).
 (9) C. L. Wendt and M. Farnsworth, *THIS JOURNAL*, **47**, 2494 (1925).
 (10) P. Jolibois, H. Lefebvre and P. Montagne, *Compt. rend.*, **186**, 648 (1928).
 (11) H. Hunt and W. C. Schumb, *THIS JOURNAL*, **52**, 3152 (1930).
 (12) P. Jolibois, *Compt. rend.*, **199**, 53 (1934).
 (13) W. C. Schumb and F. A. Bickford, *THIS JOURNAL*, **58**, 1038 (1936).
 (14) N. B. Bhatt and S. K. K. Jatkar, *J. Indian Inst. Sci.*, **20A**, 25 (1937).
 (15) V. Spreter and E. Briner, *Helv. Chim. Acta*, **32**, 2044 (1949).
 (16) F. Fischer, H. Kuster and K. Peters, *Brennstoff Chem.*, **11**, 300 (1930).
 (17) W. Manchot and W. Kampschulte, *Ber.*, **40**, 2891 (1907).

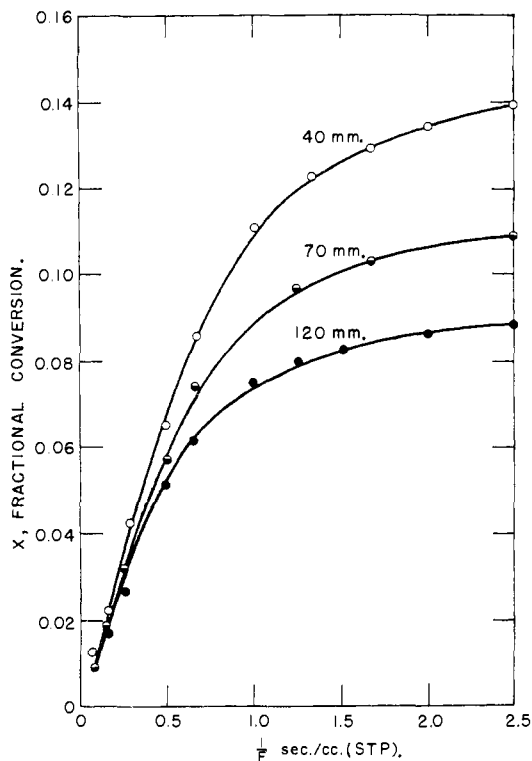


Fig. 1.—Pressure-flow rate data with the following variables kept constant: frequency, 3.0 Mc.; electrode gap distance, 6.1 mm.; current, 115 ma.

The kinetic mechanistic aspects of the CO₂ system have many points in common with combustion schemes for carbon monoxide as discussed by many workers and recently by Laidler and Griffing.¹⁹

TABLE I

Variable	Range
Pressure, mm.	30-150
Flow rate, cc./sec. (S.T.P.)	0.4-11
Current, ma.	80-180
Voltage, v.	520-830
Frequency, Mc.	1.5-6.5
Power factor	Assumed to be unity ^{2,3}
Electrodes	
Material	Nickel
Gap distance, mm.	1-12

Primary Processes.—The initial assumption is made that primary electron collisions occur only with CO₂. The dissociative impact (without ionization) of the electrons with CO₂ will most likely result in CO in its ground state (¹Σ) and O atoms in both the ground state (³P) and the low-lying excited state (¹D). Excitation of CO is not considered, since the first excited state lies 137 kcal. above the ground state and does not compare energy-wise with the excited states of other species under consideration. Similarly, the dissociation of CO₂ into three atoms, C + O + O, would require more energy (16.5 e.v.) than ionization (13.9 e.v.) and is therefore not considered. The most likely

(19) K. J. Laidler and V. Griffing, "Third Symposium on Combustion, Flames, and Explosion Phenomena," The Williams and Wilkins Co., Baltimore, Md., 1949, p. 432.

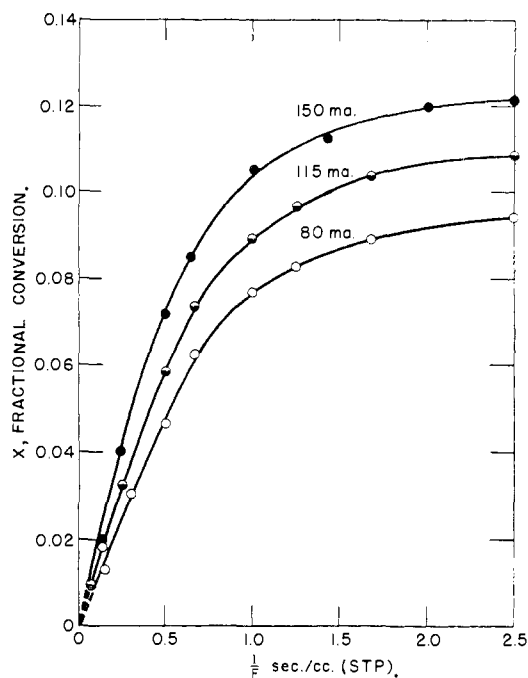
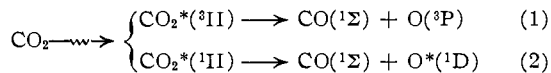


Fig. 2.—Current-flow rate data with the following variables kept constant: frequency, 3.0 Mc.; electrode gap distance, 6.1 mm.; pressure, 70 mm.

steps in the primary excitation (without ionization) are



Here, the ³II and ¹II states are the two low-lying ones predicted by Mulliken.²⁰ The minimum energy requirements for the two processes are 126 and 172 kcal./mole, respectively.

For the primary process of ionization, the mass spectrum studies on CO₂²¹⁻²³ indicate that the parent ion, CO₂⁺, is the most important, appearing at 13.9 e.v. All other ions, namely, CO⁺, O⁺ and O₂⁺, have considerably larger appearance potentials (20 e.v. or higher). In comparison, at the field strength-pressure ratios used (ca. 25 volts/cm.-mm.) in this study, the average kinetic energy of the electrons in the discharge is probably of the order of 5 e.v.²⁴ Thus, it appears that the CO₂⁺ is the ion primarily responsible for maintaining the arc and the only ion that needs to be considered in any proposed mechanism. The absence of carbon suboxide and free carbon normally found in CO discharge²⁵⁻²⁷ indicate negligible concentrations of CO⁺ and further supports the assumption that only CO₂ undergoes initial inelastic electron collisions. Since negative ions are not observed in CO₂

(20) (a) R. S. Mulliken, *J. Chem. Phys.*, **3**, 720 (1935); (b) E. C. Y. Inn, K. Watanabe and M. Zelikoff, *ibid.*, **21**, 1648 (1953).

(21) H. D. Smyth and E. C. G. Stueckelberg, *Phys. Rev.*, **36**, 472 (1930).

(22) H. Kallmann and B. Rosen, *Z. Physik*, **61**, 61 (1930).

(23) T. Kambara, *Proc. Phys. Soc. Japan*, **2**, 158 (1947).

(24) K. G. Emeleus, R. W. Lunt and C. A. Meek, *Proc. Roy. Soc. (London)*, **A156**, 394 (1936).

(25) R. W. Lunt and L. S. Mumford, *J. Chem. Soc.*, 1711 (1929).

(26) M. Crespi and R. W. Lunt, *ibid.*, **127**, 2052 (1925).

(27) N. R. Campbell, *Phil. Mag.*, [6] **42**, 227 (1921).

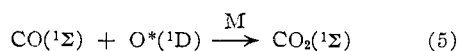
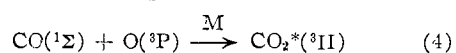
either mass spectrometrically or in retarding potential studies,²⁸ they have been discounted.

Secondary Processes.—At the relatively high pressures (30 to 150 mm.) encountered in this study, the electron-ion homogeneous recombination process leading to dissociation appears very likely. For the most abundant ion present in the discharge, we have

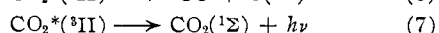
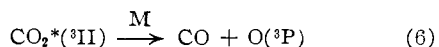


It is unlikely that unexcited CO_2 can result either by emission or through the intervention of a third body.²⁹ The electron neutralization will produce the same species as the direct dissociation (steps 1 and 2), namely: CO , O^* and O .

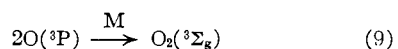
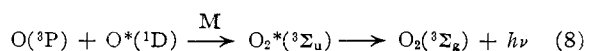
Very few plausible reactions exist among the remaining three species. CO_2 can only react with CO to give C_3O_2 , which was not found. A reaction between CO and O will regenerate CO_2 and in conformity with the spin conservation rule, both a normal and an excited CO_2 are produced



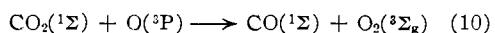
where M represents the usual third body. At these relatively high pressures ternary gas-phase collisions may be more important than wall effects. This was demonstrated by experiments of the classical Reynolds type whereby flow patterns indicated that the incoming and outgoing gas streams did not mix with the bulk of the gas in the discharge tube (water impregnated with KMnO_4 at the same Reynolds number as the critical CO_2 gas flow was passed through the discharge tube, enabling the flow pattern to be observed visually). The excited ^3II state of CO_2 in step 4 will either return to the ground state by redissociation or emission



Since chemical (without dissociation) and physical quenching require a triplet molecule, such as O_2 , which is not present in appreciable quantities, it appears that steps 6 and 7 govern the concentration of excited CO_2 (^3II) molecules in the discharge. The fate of atomic oxygen will be regulated by the combinations



One other possible secondary process is the reaction of oxygen atoms with normal CO_2



and



Reaction 10 is endothermic by 9 kcal., and since it has an activation energy of at least this amount, it will be disregarded. Reaction 11, however, is exothermic by 15 kcal. It is necessary that O_2 be formed in a singlet state for spin conservation, and

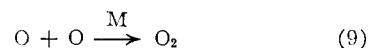
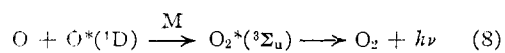
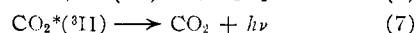
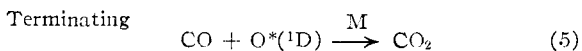
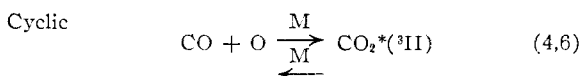
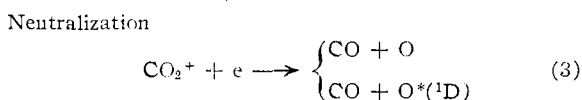
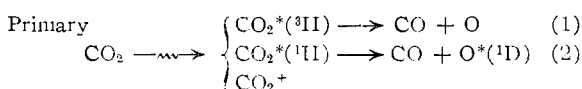
(28) N. Bradbury and E. Tatel, *J. Chem. Phys.*, **2**, 836 (1934).

(29) I. S. Møsses, *Disc. Faraday Soc.*, **12**, 24 (1952).

so the $^1\Delta_g$ state, lying 22 kcal. above the ground state is the most likely.

The exact importance of step 11 relative to the $\text{CO}-\text{O}$ reactions, (4) and (5), is not easily assessed. From direct photochemical evidence reaction 4 is known to have an activation energy of about 2 kcal.,^{19,30} whereas reaction 5 has essentially a zero activation energy.³¹ If the CO_2-O^* reaction has an appreciable activation energy (6–10 kcal.), which is very likely since bonds need to be broken and reformed, it is probably slower compared to the recombination reactions 4 and 5. Although the latter reactions require a third body, at the higher pressures employed in this study the condition does not appear to be stringent.

To summarize: the most likely elementary steps consistent with the assumptions and with the conditions of the discharge are



The foregoing reactions, possibly including the CO_2-O^* reaction,¹¹ constitute the chemical scheme which should describe the decomposition of CO_2 .

Discussion of Mechanism and Results

The hydrodynamic model taken in correlating the individual processes with the experimental data will be the usual one for practical kinetic studies in flow systems: one-dimensional flow with no mixing or diffusion.³² Processes such as ionization, excitation and recombination are treated formally in terms of conventional rate constants and concentrations. A steady-state treatment for the complete scheme of reactions as postulated in the previous section is practically not possible. An inspection of the above scheme will show, however, that the main features may be expressed in a small number of reactions representing production of active species, decomposition of the active species to give CO and O , and recombination of CO and O . Of the large number of possible mechanisms that were considered only three "sub-schemes" are characterized by these features and will be examined more closely. These are shown in Table II. Expressions for the rate of disappearance of CO_2 are easily derived, and as an example the results are given in some detail for scheme I.

(30) W. F. Jackson, *THIS JOURNAL*, **56**, 2631 (1934).

(31) B. Popov, *Acta Physicochem., U.S.S.R.*, **3**, 223 (1935).

(32) H. M. Hulburt, *Ind. Eng. Chem.*, **36**, 1012 (1944).

TABLE II

	Reaction scheme	Rate expression
I	$\text{CO}_2 \xrightarrow{\text{h}\nu} \text{CO}_2^+ + \text{e}^-$	k_1
	$\text{CO}_2^+ + \text{e}^- \rightarrow \text{CO} + \text{O}$	k_2
	$\text{CO} + \text{O} \xrightarrow{\text{M}} \text{CO}_2^* \rightarrow \text{CO}_2 + \text{h}\nu$	k_3
	$\text{O} + \text{O} \xrightarrow{\text{M}} \text{O}_2$	k_4
II	$\text{CO}_2 \xrightarrow{\text{h}\nu} \text{CO}_2^+$	$\frac{dx}{d(1/F)} = \frac{A'(1-x)}{(1 + \frac{1}{2}x)(1 + B' \frac{x}{1-x})}$
	$\text{CO}_2^+ + \text{e}^- \rightarrow \text{CO} + \text{O}^*$	
	$\text{CO} + \text{O}^* \xrightarrow{\text{M}} \text{CO}_2$	
III	$\text{CO}_2 \xrightarrow{\text{h}\nu} \text{CO} + \text{O} \text{ and } \text{O}^*$	$\frac{dx}{d(1/F)} = A'' \left(\frac{1-x}{1 + \frac{1}{2}x} \right)^2 \left[\left(1 + B'' \left(\frac{1 + \frac{1}{2}x}{1-x} \right)^{1/2} - 1 \right) \right]$
	$\text{CO}_2 \xrightarrow{\text{h}\nu} \text{CO}_2^+$	
	$\text{CO}_2^+ + \text{e}^- \rightarrow \text{CO} + \text{O} \text{ and } \text{O}^*$	
	$\text{CO}_2 + \text{O}^* \rightarrow \text{CO} + \text{O}_2$	
	$\text{O} + \text{O}^* \xrightarrow{\text{M}} \text{O}_2^* \rightarrow \text{O}_2 + \text{h}\nu$	
	$\text{O} + \text{O} \xrightarrow{\text{M}} \text{O}_2$	

The usual steady-state assumption gives for the velocity of decomposition of CO₂

$$-\frac{d(\text{CO}_2)}{dt} = k_1 n_e (\text{CO}_2) - \frac{k_3^2}{4k_4} (\text{CO})^2 M \left[\left\{ 1 + \frac{8k_1 k_4 n_e (\text{CO}_2)}{k_2^2 (\text{CO})^2 M} \right\}^{1/2} - 1 \right] \quad (12)$$

where *n_e* represents electron density and *M*, the third body concentration. From the hydrodynamic model chosen equation (13) relating conversion and flow rate is obtained

$$\frac{dx}{d(1/F)} = -V_r \frac{d(\text{CO}_2)}{dt} \quad (13)$$

where *x* represents fractional conversion, *F*, flow rate (moles/sec.) and *V_r* the effective reaction volume. The concentrations on the right-hand side of eq. 12 are expressed in moles/cc. and may be written as the product of the moles/(initial mole) and the molar density, that is

$$c = \rho x$$

Here ρ is given by $\rho_0/(1 + \omega x)$, where ω is the net increase in the number of moles per mole of CO₂ "reacted." If CO₂ and CO are the only species present in quantity, then (CO₂) is proportional to (1 - *x*) and (CO) to *x*.

Equation 13 may now be written as

$$\frac{dx}{d(1/F)} = \frac{A(1-x)}{(1 + \frac{1}{2}x)} - \frac{Bx^2}{(1 + \frac{1}{2}x)^2} \left[\left\{ 1 + \frac{C(1-x)(1 + \frac{1}{2}x)}{x^2} \right\}^{1/2} - 1 \right] \quad (14)$$

with $\omega = 1/2$ for the present case. *A*, *B* and *C* are constants which are functions of pressure, temperature and electron density. They will be discussed later in connection with the observed pressure and current dependence. Equation 14, if integrated, would give a relation between conversion *x*, and flow rate *F*, other conditions being constant. As an approximation, since *x* has a maximum value of about 0.1, average values of $\langle 1 - x \rangle$ and $\langle 1 + 1/2 x \rangle$ may be employed. Also, if the quantity $C(1 - x)(1 + 1/2x)/x^2$ is large compared to unity, as

order of magnitude calculations indicate, eq. 14 reduces to the form

$$\frac{dx}{d(1/F)} \simeq D - Ex \quad (15)$$

where *D* and *E* are new constants expressed in terms of *A*, *B*, *C*, $\langle 1 - x \rangle$ and $\langle 1 + 1/2x \rangle$. By direct integration of eq. 15 with the limits *x* = 0 and 1/*F* = 0, i.e., zero conversion at infinitely fast flow rates, the following relation is obtained for fractional conversion as a function of flow rate

$$x = \frac{D}{E} (1 - e^{-E/F}) \quad (16)$$

This expression satisfies the general trend of the curves shown in Figs. 1 and 2. Furthermore, eq. 15 predicts a straightline relationship between $\ln dx/d(1/F)$ and reciprocal flow rate, as shown in Fig. 3 for the 70 mm. pressure data taken from Fig. 1. Except for low values of *x*, the agreement is reasonably good. Unfortunately, the approximations used in deriving eq. 16 are not to blame for the poor fit at low values of 1/*F*. This was tested by a numerical analysis with the complete eq. 14. It appears that at large flow rates either alterations in the chemical mechanism of Scheme I occur, or turbulent effects possibly play a role. It is encouraging that this particular mechanism with use of a simple one-dimensional hydrodynamic model reproduces the data at lower flow rates for a considerable range of values.

The constants derived from Fig. 3 were used in eq. 16 to compare with the 70 mm. pressure data of Fig. 1. This is shown in Fig. 4, fitting the curve at the point, 1/*F* = 1.0. The fit is surprisingly good in view of the simplicity of the model employed.

The question of whether the primary process involves mainly ions or excited molecules cannot be answered in the case of CO₂, for the resulting species, CO and O or O*, are the same in either case. The relative importance and necessity of secondary steps, however, can be investigated as given below.

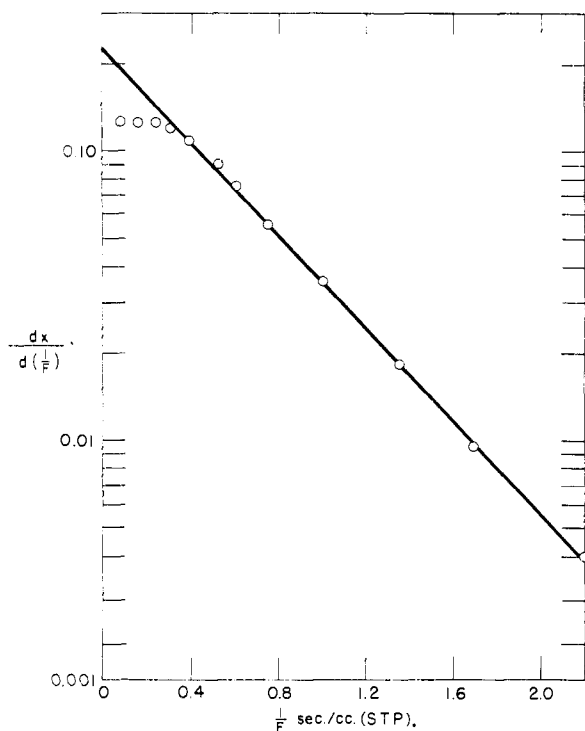


Fig. 3.

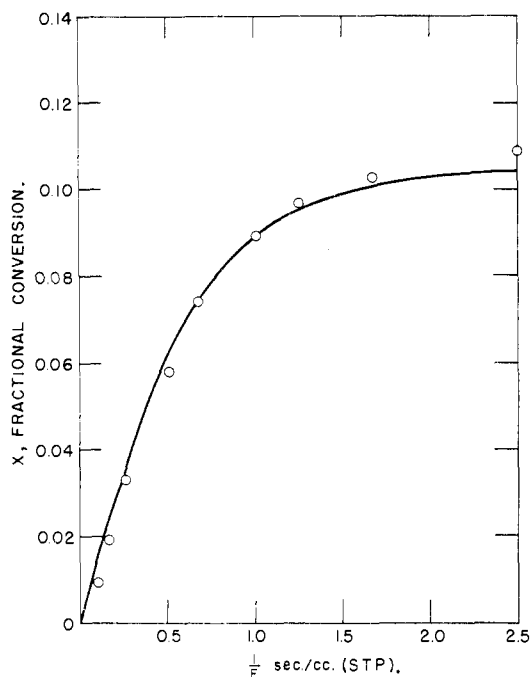


Fig. 4.—70 mm. pressure-flow data analyzed on basis of Scheme I.

A reaction scheme, such as II (see Table II), involving the $\text{CO}_2\text{-O}^*$ reaction as a terminating step rather than the O-O or O-O^* of Scheme I, may be postulated. Another primary step involving direct dissociation could be used in Scheme II, but the resulting algebraic form of the rate equation would be the same as for the steps used. The rate expression for Scheme II can be integrated exactly

to give a relation between flow rate and conversion. For analytical purposes, the usual approximations reduce the equation to

$$\frac{1}{F} \approx C'x + D'x^2 \quad (17)$$

where C' and D' involve A' , B' , V_r and numerical constants. Equation 17 was tested in Fig. 5 for the same data as used in Fig. 4. It is seen that

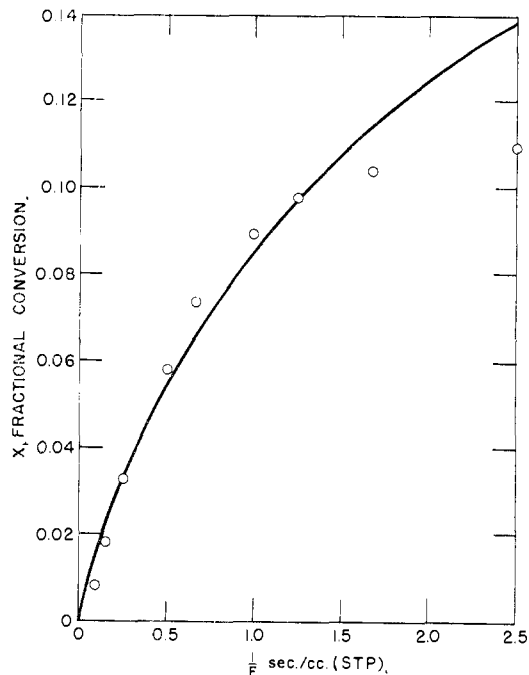


Fig. 5.—70 mm. pressure-flow data analyzed on basis of Scheme II.

the general trend is followed, but the x vs. $1/F$ curve rises much too sharply at high values of x if it is made to fit at low x . This supports the suggestion that the inclusion of the $\text{CO}_2\text{-O}^*$ reaction is of questionable merit.

If the CO-O step is eliminated a scheme such as III (see Table II) might be used, resulting in an equation of the form

$$-\frac{d(\text{CO}_2)}{dt} = A''(\text{CO}_2)^2 \left[\left\{ 1 + \frac{B''}{(\text{CO}_2)} \right\}^{1/2} - 1 \right] \quad (18)$$

Equation 18 cannot possibly explain the data for it depends only on the CO_2 concentration, that is, $(1-x)$ which is virtually constant. As seen in eqs. 14 and 17, the equation for $-d(\text{CO}_2)/dt$ must involve x directly. The above analysis adds further weight to Scheme I.

Only a qualitative discussion of the pressure and current dependence can be given, since many of the parameters such as the "rate constant" for the primary process and n_e , the electron density, have ill-defined pressure, current or field-strength dependence. However, an analysis based on eq. 12, gives added confidence in the applicability of Scheme I to the decomposition of CO_2 . According to eq. 12, the initial rate (when $x = 0$) should be proportional to n_e , and hence to current, while the rate should be *less* for smaller n_e at a given conversion, due to the n_e term inside the brackets. An

inspection of Fig. 2 will show this to be the case. The slopes of the curves for the three different currents start out proportional to the current, but at high $1/F$ values the slopes are about the same. The ratios of the initial slope to the current value, in arbitrary units, for the three curves are 0.9, 1.0 and 1.1. The slopes were found by inspection and considering the crudeness of the model, the proportionality is quite satisfactory.

The pressure dependence is a difficult one to predict. The k_1 of eq. 12 is pressure dependent because it is a function of the field strength/pressure ratio, X/p . In terms of the activation cross-section (for ionization or excitation, as the case may be), $Q(V)$, and the electron velocity-distribution function, $f(V)$, where V represents the electron energy²⁴

$$k_1 = \int Q(V)V^{1/2}f(V)dV \quad (19)$$

The integration extends over all values of V for which Q and f have appreciable values simultaneously. The pertinent point for this discussion is that k_1 is a strong function of X/p . In the range of X/p used in the present work k_1 increases with X/p , according to semi-empirical calculations on H_2 by Massey and Burhop.³³ Thus, k_1 would decrease with increasing pressure at constant field strength. From Fig. 1 it is seen that the initial rate, that is, the product $k_1n_e(\text{CO}_2)$, is virtually independent of pressure. Since (CO_2) and n_e are proportional to pressure, k_1 must be roughly inversely proportional to the square of the pressure. Figure 1 also indicates that the slope of the $x - 1/F$ curves is greater for lower pressures. This can be rationalized on the basis of eq. 12. The second term is approximately proportional to $(\text{CO})M^{1/2}$, that is, to the three-halves power of the pressure, provided that the product $k_1n_e(\text{CO}_2)$ is pressure-independent. Thus even though the initial rate is independent of pressure the subsequent rate should

(33) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," The Clarendon Press, Oxford, 1952, p. 237.

be inhibited at higher pressures, for a given flow rate. This is also consistent with the observed decrease in decomposition with pressure, for a given flow rate.

Conclusion

The foregoing results indicate that it is possible to explain chemical effects in electric discharges in terms of the kinetics of elementary chemical reactions. This is further confirmed by the recent papers of Burton^{34,35} and his collaborators. As can be seen from Fig. 3, any proposed scheme must give a relationship for $dx/d(1/F)$ of the form of eq. 15. It has been shown that replacing the oxygen atom combination step with the $\text{CO}_2\text{-O}^*$ step as in Scheme II gives a poor fit of the data and similarly it was also found that the CO-O type step, which was omitted from Scheme III, must be included. No kinetic scheme without this elementary step could explain the experimental results. The apparent inertness of carbon dioxide to high energy radiation in static systems is probably due to this recombination reaction.

It is not possible at the present time to present a complete verification of a given step or series of steps in any kinetic scheme. Final justification of any mechanism requires a detailed study of individual steps. From gross kinetic studies, the most that can be done is to outline the likely elementary reactions by means of spectroscopic, thermodynamic and kinetic considerations, and compare the results of various schemes through a simple hydrodynamic model of the discharge. The inclusion of a given species, such as ions, must be justified on the basis of the foregoing procedure, where each system is considered on its own merits.³⁶

(34) H. Wiener and M. Burton, *THIS JOURNAL*, **75**, 5815 (1953).

(35) J. C. Devins and M. Burton, *ibid.*, **76**, 2618 (1954).

(36) E. G. Zubler, Wm. H. Hamill and R. R. Williams, Jr., *J. Chem. Phys.*, **23**, 1263 (1955).

WASHINGTON, D. C.