

trodes fractured in repolishing, all could not be used for the same number of runs. The results of each determination were given equal weight, the Pierce-Chauvenet Criteria⁷ being used to decide whether an observation was to be rejected. Treatment of the data by the method of least squares gives the relationship

$$E = 0.349 - 0.0469pH \quad (2)$$

The probable deviation of any single result from the value predicted by (2) is less than 0.005 volt.

If the contribution of the saturated calomel electrode and associated liquid junction is assumed to be -0.244 v. (oxidation potential),⁸ the reduction potential for the tellurium—tellurium oxide couple becomes

$$E' = 0.593 - 0.0469pH \quad (3)$$

At 20° in the pH range 0 to 9 Tomíček and Poupe⁶ report

$$E' = 0.603 - 0.058pH \quad (4)$$

These workers employed mechanically polished tellurium electrodes and oxygen-saturated buffer solutions. If, in oxygen saturated solutions, tellurium behaves as an oxygen electrode, the theoretical slope would be 0.059 at 25°. Preliminary measurements do indicate a positive oxygen effect; the e.m.f. of the cell does increase when oxygen is bubbled through the system. Passage of nitrogen has negligible effect on the e.m.f. of the cell.

The lack of agreement of potential-pH relationships of metal-metal oxide electrodes among vari-

(7) T. Crumpler and J. Yoe, "Chemical Computations and Errors," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 190.

(8) H. Harned and B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., A.C.S. Monograph 95, Reinhold Publ. Corp., New York, N. Y., 1950, p. 320.

ous workers is well known. Tourky and Moussa⁹ have summarized the relationships from twenty-five investigations of the antimony-antimony oxide electrode; the slopes and intercepts ranged from 0.043 to 0.0647 and from 0.151 to 0.290, respectively.

Brief studies of the suitability of both the cast and the electroplated amorphous tellurium electrodes in acid-base titrimetry also were made. In the titration of HCl or acetic acid with NaOH, the equivalence points obtained, respectively, with the glass and the tellurium electrodes agreed to $\pm 0.5\%$. Contrary to the findings of Brouwer¹⁰ and Bravo¹¹ who claimed that potential stabilization of the tellurium-calomel couple was not attained for two or three hours after each addition of base, our electrodes stabilized in a few minutes. At a pH greater than 10, however, stability could not be realized.

In solution tellurium dioxide is a weak ampholyte; its isoelectric point occurs at a pH of 4.2.¹² Thus the dissociation of the basic form is not the simple $\text{Te}(\text{OH})_4 = \text{Te}^{+4} + 4\text{OH}^-$ as postulated by Kasarnowsky.¹³ A calculation of the standard electrode potential of the Te/TeO₂ half cell cannot be made satisfactorily. Further studies of this electrode system are being made using cells without liquid junction.

Acknowledgments.—The authors wish to thank the Research Corporation of America for the funds that were used to support this work.

(9) A. Tourky and A. Moussa, *J. Chem. Soc.*, 752 (1948).

(10) St. de Brouwer, *Bull. soc. chim. Belg.*, 48, 158 (1938).

(11) A. Bravo, *Ann. chim. applicata*, 26, 182 (1936).

(12) I. Assa and S. Awad, *J. Phys. Chem.*, 58, 948 (1954).

(13) J. Kasarnowsky, *Z. physik. Chem.*, 109, 287 (1924).

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

Photochemical Studies. LIV. Methanol Vapor¹

BY RAYMOND P. PORTER AND W. ALBERT NOYES, JR.

RECEIVED SEPTEMBER 27, 1958

The principal products of the photochemical decomposition of methanol vapor at wave lengths below 2000 Å. are hydrogen, formaldehyde, ethylene glycol together with small amount of carbon monoxide and methane. By use of scavengers and by study of deuterated methanol, CD₃OH, it is shown that there are at least two primary processes, one of which must be $\text{CH}_3\text{OH} + h\nu = \text{CH}_3\text{O} + \text{H}_2$. One process must give hydrogen atoms. Secondary reactions are discussed.

The thermal decomposition,² the direct photochemical decomposition,³ and the mercury sensitized decomposition⁴ of methanol vapor have been studied. Patat and Hoch³ concluded that the

(1) This research was supported in part by contract AF18(600) 1528 with the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command. Reproduction in whole or in part is permitted for any purpose by the United States Government. The authors wish to express their appreciation to Dr. P. Ausloos for many helpful discussions and ideas. Further details on experimental procedures may be obtained from the Ph.D. Thesis of Raymond P. Porter, University of Rochester, 1958.

(2) W. A. Bone and H. Davies, *J. Chem. Soc.*, 105, 1691 (1914); E. Peytral, *Compt. rend.*, 165, 703 (1917); J. M. C. Fletcher, *Proc. Roy. Soc. (London)*, 147A, 119 (1934).

(3) F. Patat and H. Hoch, *Z. Elektrochem.*, 41, 494 (1935).

(4) H. S. Taylor and J. R. Bates, *THIS JOURNAL*, 49, 2438 (1927); M. K. Phibbs and B. de B. Darwent, *J. Chem. Phys.*, 18, 495 (1950).

primary process for direct photochemical decomposition was into formaldehyde and hydrogen. Hydrogen and formaldehyde were found to be produced in equal amounts. Rough measurements indicated a quantum yield of 1.1 for hydrogen formation. A heavy wall deposit was formed, however. The results on the mercury sensitized reaction are best explained by the initial formation of CH₂OH radicals and hydrogen atoms.

Fricke and Hart⁵ and Farkas and Hirschberg⁶ found the ultraviolet irradiation of aqueous solutions of methanol to give mainly hydrogen and formaldehyde. Differences in results and in interpretation need not be discussed here.

(5) H. Fricke and E. J. Hart, *ibid.*, 4, 418 (1936).

(6) L. Farkas and Y. Hirschberg, *THIS JOURNAL*, 59, 2450 (1937).

The radiolysis of methanol and of aqueous methanol solutions has been studied.^{5,7}

Takezaki and Takeuchi⁸ induced decomposition of methanol by methoxy radicals formed from the thermal decomposition of dimethyl peroxide. Methoxy radicals seem to react readily with methanol to give CH_2OH radicals, a result to be anticipated from the work of Wijnen.⁹

It is difficult to draw many conclusions about the primary photochemical process in methanol from previous work. Further work on this matter was needed.

Experimental

It has been shown already by Porter¹⁰ that methanol vapor in contact with boron containing glass may accumulate high mole percentages of trimethyl borate, $\text{B}(\text{OCH}_3)_3$. As much as 12 mole % trimethyl borate was found in methanol vapor which had been allowed to stand in Pyrex glass for several hours. Trimethyl borate would hydrolyze if water were present.

Before the presence of trimethyl borate was suspected, results were not reproducible. Since trimethyl borate absorbs more strongly than methanol at the wave lengths used, the lack of reproducibility was due almost certainly to varying amounts of trimethyl borate. It was necessary to purify the methanol and to perform experiments in a glass-free system. It was necessary to use a mercury free system to avoid the possibility of mercury sensitized reactions.

Two samples of Mallinckrodt acetone free analytical reagent grade methanol were used. One sample of alcohol was distilled in a nitrogen atmosphere in a Vycor column from a mixture of methanol, iodine and aqueous sodium hydroxide and then distilled over magnesium. The methanol finally was vacuum distilled over fused silver nitrate. The other sample was distilled twice over magnesium and then vacuum distilled. The two samples gave identical results.

The Cary spectrophotometer showed no absorption, in either sample, of the methanol vapor at 100 mm. pressure in an 8 cm. path length. Mass spectra showed no peaks greater than 34. The formaldehyde content determined by the method of Matsukawa¹¹ was from 1.0 to 2.5 micrograms per milliliter.

Deuterated methanol, CD_3OH , was obtained from the Merck Company of Canada. Impurities were diminished by treating with Eastman Kodak Company White Label furfural and a small amount of aqueous sodium hydroxide followed by distillation three times at -35 , -40 and -50° , respectively. The mass spectrogram indicated possibly a slight impurity, but a Perkin-Elmer Vapor Fractometer showed no impurities.

Methanol CH_3OD , also obtained from the Merck Company of Canada, contained about 0.1% xylene, and it proved to be impossible to purify and use this material.

Deuterium hydride was prepared by condensing D_2O (99.5% obtained from the Stuart Oxygen Company) with sodium borohydride (98+ % from Metal Hydrides Co.).¹² The deuterium hydride formed on warming was passed through a trap immersed in liquid nitrogen and used without further purification.

Deuterium (99.5% from the Stuart Oxygen Company) was passed through a trap immersed in liquid nitrogen and used without further purification.

Hydrogen was purified by passage through a palladium thimble. Oxygen was prepared by heating potassium permanganate. These two gases were passed through a trap immersed in liquid nitrogen. Phillips Petroleum Company research grade ethylene was used. It was outgassed by pumping on it while frozen with liquid nitrogen. Reagent grade carbon dioxide was obtained from the Air Reduction Sales Company.

(7) W. R. McDonnell and S. Gordon, *J. Chem. Phys.*, **23**, 208 (1955); W. R. McDonnell, *ibid.*, **23**, 208 (1955).

(8) Y. Takezaki and C. Takeuchi, *ibid.*, **22**, 1527 (1954).

(9) M. H. J. Wijnen, *ibid.*, **27**, 710 (1957); **28**, 271 (1958).

(10) R. P. Porter, *J. Phys. Chem.*, **61**, 1260 (1957).

(11) D. Matsukawa, *J. Biochem. (Tokyo)*, **30**, 386 (1939).

(12) The authors wish to thank Professor W. H. Saunders for suggesting this method of preparation.

A Consolidated-Vacuum all metal, two stage diffusion pump was used with Dow Corning 703 diffusion pump fluid. The portion of the line used for storage and photolysis was made of quartz, copper tubing and metal valves.

The cell used for most of the runs was made of quartz, 2.17 cm. in diameter and 19.9 cm. in length. The total volume including leads was 136.8 ml. The cell was mounted in an asbestos wrapped aluminum furnace which protruded 1 cm. over the ends of the cell. The rear window was insulated. Cell temperature was read on a calibrated thermometer inserted in a well drilled in the aluminum block.

The cell transmitted through 3 cm. of air to at least 1835 Å.

In some experiments a cell 4.8 cm. in diameter and 8.1 cm. in length was used. Total volume including leads was 179.3 ml.

Most of the runs were made with a Hanovia No. 71A32 hydrogen lamp operated on a 5000 v., 2.5 kva transformer. Within about 3% the intensity, as measured by rate of production of gases non-condensable by liquid nitrogen, was proportional to the current through the lamp.

Heated air was blown between the lamp and the cell to remove ozone. In some runs nitrogen flowed through a tube 1.8 cm. in length inserted between the lamp and the cell.

The section used to transfer product gases was designed to prevent entrance of mercury vapor into the cell system.

The analytical system was similar to that described in previous publications.¹³ Gases not condensed by liquid nitrogen were analyzed either by combustion over copper oxide or by the mass spectrometer (Consolidated Engineering Company Model 21-620). Carbon monoxide was determined by peak 28 and methane by peak 16. Hydrogen was taken as the difference between total non-condensables and the sum of methane and carbon monoxide.

The deuterated methanol gave deuterated methanes, and it was assumed that these have the same sensitivity for parent peaks as for CH_4 itself. Analyses for H_2 , HD and D_2 were subject to larger errors than were the other analyses. This was particularly true if other gases were present. Calibration runs were made with known ratios of the three hydrogens in the presence of foreign gas, mainly air, at definite pressures. Corrections were made for the variation in sensitivity of the hydrogen peaks. Since the sensitivities were not the same for the three peaks, it is possible that the rate of diffusion into the spectrograph played an important part. This introduces a small element of uncertainty in the determination of three types of hydrogen.

Products of three runs were analyzed with a Perkin-Elmer Model 154-B Vapor Fractometer with column "A" two meters in length. Formaldehyde was determined by the method of Matsukawa.¹¹

Several methods of determining small quantities of ethylene glycol in the presence of a large amount of methanol were tried. The mass spectrometer is not very sensitive for this compound and the Vapor Fractometer proved to be unreliable. The method used involved the oxidation of the glycol to formaldehyde by potassium periodate, precipitation of excess periodate by silver nitrate and precipitation of excess silver by sodium chloride. The formaldehyde produced by the oxidation then was determined by the method of Matsukawa.¹¹ Prolonged oxidation resulted in some decrease in formaldehyde, *i.e.*, after one week about 75% remained.

Results

Complete analyses were made for three runs. The analysis for ethylene glycol was laborious and was not performed for the rest of the runs. In view of the results in Table I which show a hydrogen atom to carbon atom ratio of nearly four in the known products it was assumed that all of the principal products were known. Where necessary the amount of ethylene glycol was calculated from the amounts of the other products.

Since absolute quantum yields were not determined, trends in the results are more important than actual numerical data. The main results are shown in Figs. 1, 2 and 3.

(13) A. N. Strachan and W. A. Noyes, Jr., *THIS JOURNAL*, **76**, 3258 (1954).

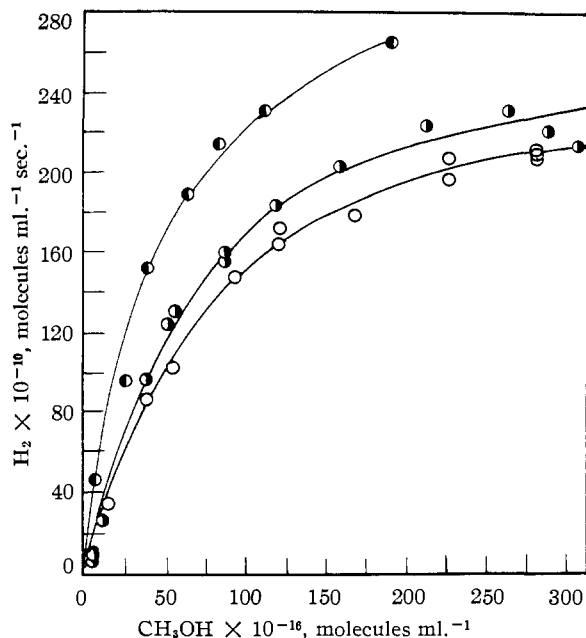


Fig. 1.—Variation of hydrogen with pressure: O, 30°; ◐, 50°; ●, 175°.

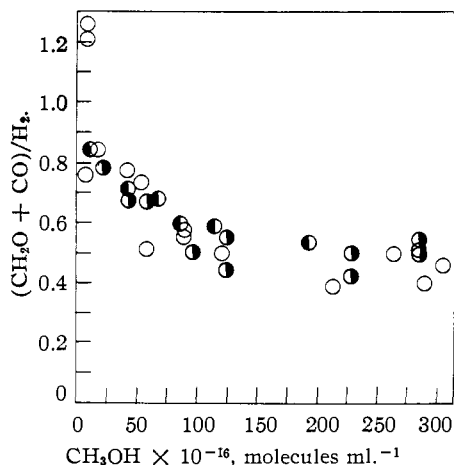


Fig. 2.—Variation of formaldehyde plus carbon monoxide/hydrogen with pressure: ●, 30°; O, 50°; ◐, 175°.

The increase in rate of hydrogen production with increase in temperature probably is due mainly to increase in absorption with temperature. The wave lengths used lie mainly between 1800 and 2000 Å., which is on the long wave end of a general absorption region that appears to be a continuum.^{14,15} An increase in temperature should lead to an increase in absorption. There are two maxima at 54500 and 63700 cm.^{-1} , respectively with a minimum at 60300. It is possible that primary processes on the two sides of the minimum are different, but the data do not prove this to be the case. An air filter between the lamp and the cell should change the wave length distribution of the absorbed light, but the ratio of non-condensables to formaldehyde did not change when air was substituted for nitrogen. More than one primary

(14) G. Herzberg and G. Scheibe, *Z. physik. Chem.*, **7**, 390 (1930).

(15) A. J. Harrison, Office of Naval Research, Report from Project NR-055-160.

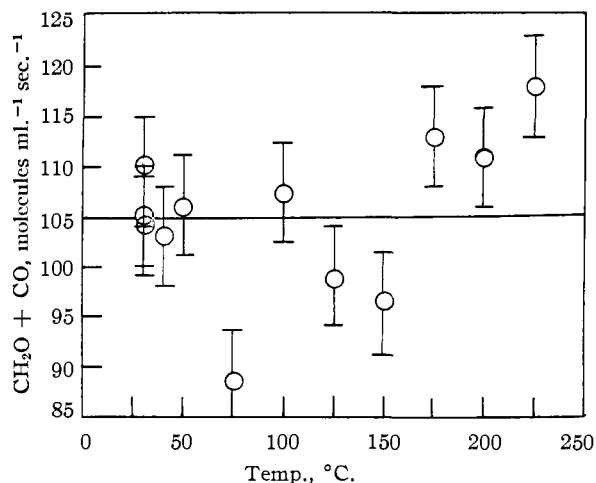


Fig. 3.—Variation of formaldehyde plus carbon monoxide with temperature corrected for increased absorption; methanol at 88.3 mm. pressure.

process must occur in the long wave absorption region.

Small amounts of methane and of carbon monoxide always were produced. Carbon monoxide can be explained by some photochemical decomposition of formaldehyde since the absorption by the latter is very much higher than that of the alcohol itself. In some runs (data not shown) it is clear that the amount of carbon monoxide increases with extent of decomposition. In calculations of the total formaldehyde, carbon monoxide was always added to formaldehyde. The

TABLE I

MATERIAL BALANCE

Large cell; $P_{\text{CH}_3\text{OH}} = 97 \text{ mm.}$; $T = 32^\circ$; filter, air; analysis of non-condensable; copper oxide oxidation.

Length of run, hr.	Products (molecules/ml. sec.) $\times 10^{-10}$					H/C
	H ₂	CH ₄	CO	CH ₂ O	(CH ₂ OH) ₂	
2.00	491	6.26	13.1	163	295	4.02
1.88	488	6.02	14.4	128	290	4.11
1.88	552	6.10	27.0	126	354	4.04
Av.						4.05

formation of methane may be due to a reaction of hydrogen atoms with methanol, or it may be due to a small amount of dissociation into CH₃ and OH radicals. Such a dissociation is suggested for short wave lengths by the work of Terenin and Neujmin¹⁶ who found the bands of OH to be emitted when methanol was exposed to radiation below 1560 Å. The amount of methane was essentially independent of temperature, of pressure of methanol, and of time of exposure. The absolute amount was about 5.5×10^{10} molecules/ml. sec. and was less than 1% of the hydrogen in most runs. No further discussion of methane will be given.

For every formaldehyde which decomposes to give carbon monoxide, presumably one molecule of hydrogen is formed. No correction has been made for this in calculating the ratio of hydrogen to formaldehyde since carbon monoxide was always a minor product. Carbon monoxide did not become greater than 10% of the formaldehyde

(16) A. Terenin and H. Neujmin, *J. Chem. Phys.*, **3**, 436 (1935).

except for methanol pressures below 5 mm. at 30° and below 18 mm. at 175°.

The ratio of hydrogen to formaldehyde plus carbon monoxide depended upon the cell used. It was about 3 in the large diameter cell and about 2 in the small diameter cell. This may indicate some wall effect.

Experiments with CD₃OH showed H₂ and HD as the main hydrogens formed and D₂ could be detected only in long runs. This is a further indication that formaldehyde is photochemically destroyed. The H₂ was about 20% of the total.

Several experiments were carried out with added gases, particularly carbon dioxide, ethylene and oxygen. These results are summarized in Table II.

TABLE II
PHOTOLYSIS OF METHANOL IN THE PRESENCE OF ADDED GASES^a

Length of run, 90.0 min.; filter, air; cell, small diameter; pressure of methanol, 30 mm.; analysis of non-condensables, mass spectrometer; position of light source, 2.4 cm. from cell window.

Temp., °C.	Added gases	(Molecules/ml. sec.) × 10 ⁻¹⁰			
		H ₂	CH ₄	CO	CH ₂ O
175		139	2.5	6.6	70.1
175	CO ₂ 21 cm.	175	1.2	6.8	70
170	C ₂ H ₄ 4.5 cm.	60.5	0	3.7	38.2
175	C ₂ H ₄ 4.5 cm., CO ₂ 39 cm.	64.7	0	4.6	41.7
175	O ₂ 1 mm., CO ₂ 35 cm.	76
175	CH ₃ OH 0 mm., C ₂ H ₄ 4.5 cm.	18.5	0	0	..
30	C ₂ H ₄ 4.5 cm., CO ₂ 31 cm.	53	0	2	33.0
30	O ₂ 1 mm., CO ₂ 28 cm.	53

^a Before this series of runs, cell was cleaned in nitric acid. Cell window was heated to white heat, some warping of the window occurred.

The amount of hydrogen found in experiments when both oxygen and carbon dioxide were added simultaneously was about the same as the amount of formaldehyde produced without added oxygen. When ethylene was added, it absorbed to some extent to produce hydrogen. If this amount of hydrogen is subtracted, the remaining hydrogen is equal to formaldehyde plus carbon monoxide.

The addition either of oxygen or of iodine to CD₃OH suppressed D₂ formation completely and H₂ and HD were the only hydrogens produced.

TABLE III
PHOTOLYSIS OF CD₃OH IN THE PRESENCE OF ADDED GASES^a
Temperature of cell, 30°; cell, large diameters; analysis of non-condensables, mass spectrometer.

Pres- sure CD ₃ OH, mm.	Length of run, min.	Added gases	Compn. of hydrogens, %		
			D ₂	HD	H ₂
90	140	I ₂ 0.5 mm. (solid) ^b	0.0	90.5	9.5
90	107	O ₂ 1 mm.	.0	83.0	17.0
12	242	O ₂ 2 mm.	.0	81.7	18.3
12	240	CO ₂ 20 cm., O ₂ 2 mm.	.0	80	20
90	120		3.6	76.6	19.8

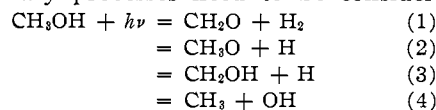
^a The authors are indebted to Dr. P. Ausloos for his aid in performing these runs. ^b The cell was closer to the light source for this run. Iodine vapor could be seen to be less concentrated toward the front window. Total hydrogen in the last run was five to ten times that in any of the other runs.

The variation of rate of hydrogen formation with pressure (Fig. 1) could be ascribed solely to increase in absorption with increase in pressure

were it not for the data shown in Figs. 2 and 3. In Fig. 2 it is seen that there is a definite trend toward a higher ratio of (CH₂O + CO)/H₂ at low pressures, and in Fig. 3 it is seen that (CH₂O + CO)/H₂ shows no very consistent trend with temperature provided the data are corrected for change in absorption as measured by hydrogen production. Hence it appears probable that hydrogen atoms react quantitatively with methanol at high pressures but that some of them fail to do so at low pressures.

Discussion

Four primary processes need to be considered



Reaction 4 may be dismissed as being of small importance due to the small yield of methane, although there is some evidence that it may be important at short wave lengths.¹⁶

The data obtained with scavengers as well as the data with deuterated methanol (CD₃OH) indicate strongly that reaction 1 is important. The reasons may be summarized as follows: (1) formaldehyde and hydrogen are both formed in the presence of scavengers; (2) the amount of hydrogen formed in the presence of scavengers is closely equal to the formaldehyde formed in their absence; (3) HD is the principal hydrogen formed from CD₃OH. Reason 3 is not decisive.

Since the ratio (CH₂O + CO)/H₂ is not unity, reaction 1 is not the sole primary process. Data with long exposures (not shown) and data from CD₃OH both show that carbon monoxide probably results from the decomposition of formaldehyde, and this decomposition undoubtedly is accompanied by some hydrogen formation (including D₂ formation in CD₃OH).

The distinction between processes 2 and 3 is difficult to make since the recent data of Wijnen⁹ show that methoxy radicals abstract hydrogens with low activation energies. Hence any CH₃O radicals produced in the primary process should rapidly form CH₂OH radicals by hydrogen abstraction. Also hydrogen atoms should form CH₂OH radicals by abstraction. On the other hand the absence of D₂ in the products, except for large conversions, argues strongly for (2) and against (3).

Some formaldehyde may be produced by disproportionation reactions or by thermal decomposition of CH₃O or CH₂OH. The data show that formaldehyde formed in this way must be small under the present experimental conditions compared with formaldehyde produced in the primary process. The thermal decomposition of either CH₃O or CH₂OH to give formaldehyde must involve an activation energy of 20 kcal. or more.⁴ In agreement with the data of Phibbs and Darwent,⁴ CH₂OH radicals seem to give mainly ethylene glycol at low temperatures.

The question of hot hydrogen atoms may be raised, but a decision about them cannot be made. One may only say that hydrogen atoms formed in the primary process seem rapidly to abstract

hydrogen probably to give CH_2OH and H_2 . The fact that hydrogen equals formaldehyde in the presence of scavengers and that the formaldehyde in the absence of scavengers is equal to the H_2 in the presence of scavengers shows that excess of hydrogen over $(\text{CH}_2\text{O} + \text{CO})$ must be due to reactions of hydrogen atoms produced in the primary process. The energy relationships are such that hot atoms could be expected from either primary process 2 or primary process 3.¹⁷

(17) P. Gray, *Trans. Faraday Soc.*, **52**, 344 (1956).

A logical interpretation of the data can be based on primary process 1 accompanied by primary process 2, followed by such reasonable reactions of the radicals and atoms as would be expected from earlier work. The arguments against some occurrence of (3) are strong but not absolutely conclusive. A more detailed discussion of the mechanism does not seem to be warranted at this time.

ROCHESTER, NEW YORK

[CONTRIBUTION NO. 2454 FROM THE GATES AND GRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Shock Waves in Chemical Kinetics: The Thermal Decomposition of NO_2 ^{1a}

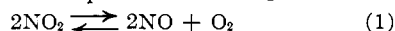
BY ROBERT E. HUFFMAN AND NORMAN DAVIDSON

RECEIVED SEPTEMBER 29, 1958

The thermal decomposition of NO_2 in argon- NO_2 mixtures has been investigated by the shock wave method, using both incident and reflected shocks. The argon: NO_2 ratio was varied from 360 to 5.6, and the temperature was varied from 1400 to 2300°K. The rate law is $-\text{d}(\text{NO}_2)/\text{d}t = k_u(\text{M})(\text{NO}_2) + k_b(\text{NO}_2)^2$. (M is the total (mainly argon) gas concentration, and $k_u = 3.06 \times 10^{13} \exp(-65,400/RT)$ mole⁻¹ liter sec.⁻¹, $k_b = 2.5 \times 10^{10} \exp(-25,000 (\pm 5000)/RT)$ mole⁻¹ liter sec.⁻¹.)

The k_u term in the rate law is believed to be due to the unimolecular dissociation at its low pressure limit $\text{M} + \text{NO}_2 \xrightarrow{k_u/2} \text{M} + \text{NO} + \text{O}$ (6), followed by $\text{O} + \text{ONO} \rightarrow \text{O}_2 + \text{NO}$ (fast), and it is shown that measurements of the reverse of reaction 6 at low temperature are in agreement with our high temperature values for k_u . The k_b term is partly due to the "Bodenstein bimolecular path." However, the values of k_b are about eight times greater than the extrapolated values for the Bodenstein mechanism; there may be some other bimolecular path which contributes to the decomposition. The results illustrate a characteristic feature of high temperature chemistry: namely, that a number of reaction paths frequently contribute to an over-all chemical transformation.

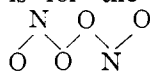
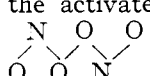
The thermal decomposition of NO_2 is in many



respects one of the classical examples of a bimolecular reaction. It was studied by Bodenstein and Ramstetter^{1b} and later by others, including Rosser and Wise.² For the rate constant between 600 and 1000°K., the latter authors give

$$-\frac{1}{(\text{NO}_2)^2} \frac{\text{d}(\text{NO}_2)}{\text{d}t} = k_{1b} = 4.0 \times 10^9 \exp(-26,900/RT) \text{ mole}^{-1} \text{ l. sec.}^{-1} \quad (2)$$

(Subscript b implies the belief that this constant is for the "Bodenstein mechanism," with the

 transition state for reaction 1.) A transition state calculation, with reasonable values for the distances and vibration frequencies of the activated complex, which is assumed to be , agrees rather well with the observed pre-exponential factor.³ (At low temperatures, the reverse termolecular reaction has a small negative temperature coefficient which has been extensively studied; above 500°K., this rate constant is essentially constant in accordance with (2).)⁴

(1a) From the Ph.D. thesis by R. E. H., California Institute of Technology, 1958.

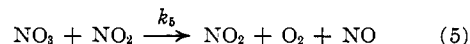
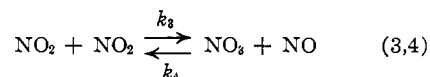
(1b) M. Bodenstein and H. Ramstetter, *Z. physik. Chem.*, **100**, 106 (1922).

(2) W. A. Rosser, Jr., and H. Wise, *J. Chem. Phys.*, **24**, 493 (1956).

(3) D. R. Herschbach, H. S. Johnston, K. S. Pitzer and R. E. Powell, *ibid.*, **25**, 736 (1956).

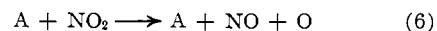
(4) H. J. Schumacher "Chemische Gasreaktionen," Theodor Steinkopf, Leipzig, 1938, pp. 311-320.

By observing the very early stages of the reaction, Ashmore and Levitt⁵ discovered that the initial rate of pyrolysis near 700°K. is greater than that observed by previous investigators; this additional contribution to the rate is quenched as NO forms or if NO is added to the initial mixture. These phenomena are attributed to the new reaction path



This proposal is consistent with the properties of NO_3 as determined in other investigations.^{6,7}

We report here a shock tube study of the rate of the same reaction in NO_2 -argon mixtures from 1400-2300°K. In addition to the bimolecular reaction path, there is a unimolecular dissociation path



There is available a brief preliminary report of another shock wave investigation.⁸ The experimental results in the two studies agree rather well; the differences in interpretation will be considered below.

(5) P. G. Ashmore and B. P. Levitt, *Research (Correspondence)*, **9**, 525 (1956).

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