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Photolysis of Acetic Anhydride

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The photolysis of acetic anhydride has been studied using a hot mercury arc at temperatures from 60° to 160°C by analysis of the gaseous products. CO and C₂H₆ are produced at equal rates which are one-half the rate of production of CO₂. At 60°C, CO production is delayed initially but in time reaches the same rate as C₂H₆. Using acetone as actinometer, the quantum yield of CO₂ is two, of CO and C₂H₆, unity. The decomposition of acetic anhydride can be photosensitized by acetone. Mass-spectral analysis of the liquid residue at 160°C showed the absence of acetone, biacetyl, methyl acetate, acetylacetone, and acetonol acetone. A fragment of mass 57, increasing in intensity with duration of reaction was present in amounts sufficient to account for a material balance. Some steps in the mechanism are discussed.

AN earlier study of the photochemical decomposition of acetic anhydride by Kandel and Taylor¹ using a mercury resonance lamp inside the reaction vessel was attributed to the absorption of 1849 Å radiation. The rate of reaction measured as a pressure change was found to be first order, though studied only over a limited pressure range. There existed a possibility that the reaction may have been, at least in part, mercury sensitized and the analytical results reported represented the products only after rather extensive decomposition, while the rate of measurements were made in terms of the pressure change occurring essentially initially. It was therefore felt that a better insight into the reaction could be obtained by an alternative study. Since acetic anhydride exhibits some absorption around 2500 Å, a medium pressure mercury lamp, in which the resonance lines are completely reversed, was used, and provision made to eliminate any 1849 Å radiation. The reaction was followed analytically over a much larger concentration range than heretofore.

EXPERIMENTAL

Acetic anhydride, after standing over metallic sodium, was distilled through a column packed with carbon rings and a fraction boiling between 138–139°C was collected in a vessel protected from moisture by anhydrous calcium sulfate. The purity of the fraction was checked by its refractive index. Later, an analysis by a mass spectrometer, showed trace amounts of acetic acid as the only impurity, and these could be attributed to hydrolysis during sampling or by moisture in the mass spectrometer. The acetic anhydride was distilled *in vacuo* into a storage bulb immersed in liquid nitrogen and separated from the reaction vessel by a mercury cutoff.

The reaction cell of 300 cc volume was cylindrical, with plane polished ends. It was mounted in an oven, whose temperature was maintained by a bimetallic

regulator. A Hanovia S.H. type quartz medium pressure mercury lamp was the source of illumination and was mounted on top of the oven about one foot above the cell. To achieve a variety of pressures of acetic anhydride vapor, the system between the cell and storage bulb was wrapped with Nichrome wire and heated. The storage bulb was heated by hot water, the temperature being determined by trial according to the vapor pressure required. The high solubility in and solvent action on stopcock grease was overcome by using mercury cutoffs wherever necessary. A conventional pumping system consisting of a two-state mercury diffusion pumped backed by an oil pump was used. The analytical system, consisting of a constant volume manometer as gas pipet and appropriate absorption pipets was similar to that used for microanalysis by Saunders and Taylor.²

The procedure for a run was as follows: after the system had been evacuated to 10⁻⁶ mm, the lamp operated for at least one-half hour to attain full intensity and the storage bulb of acetic anhydride warmed to the desired temperature, vapor was admitted to the reaction cell by lowering a mercury cutoff, the time being noted. The initial pressure to within one mm mercury, was read on a mercury cutoff functioning as a manometer, separating the cell from the analytical system. After the required exposure the reaction system was opened to a series of traps through the manometer cutoff.

The first trap was kept at -110° to -112°C using dry ice and acetone, precooled in liquid nitrogen. A second trap was maintained at -212°C using liquid nitrogen held at low pressure. The temperature was calculated from the measured vapor pressure. After standing open to the traps for at least one-half hour, noncondensables were pumped by a Toepler pump into the gas buret where the total volume was measured. Carbon monoxide was then oxidized over copper oxide at 300°C and the resulting dioxide trapped out in a cold-finger in liquid nitrogen. The remaining volume of gas was measured and the process repeated to constant volume. Only a

* Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, March, 1954.

¹R. J. Kandel and H. A. Taylor, *J. Chem. Phys.* **19**, 1250 (1951).

²K. W. Saunders and H. A. Taylor, *J. Chem. Phys.* **9**, 616 (1941).

TABLE I.

Time (min)	Temp. 80°C		Initial pressure 25 mm moles $\times 10^6$	
	CO		C ₂ H ₆	CO ₂
30	3.30		3.16	9.20
40	4.00		4.14	10.1
60	6.60		6.20	15.4
70	7.78		7.30	18.2
90	10.4		9.65	22.5

very small residual gas was found, too small for further analysis and for reasons to be shown was assumed to be methane.

The cold-finger in liquid nitrogen was warmed by replacement with dry ice acetone. This enabled any carbon dioxide to vaporize but would hold back water vapor, had there been hydrogen in the noncondensable gas. The volume of the gas was measured and the gas passed into a pipet containing ascarite. In all cases complete absorption occurred indicating that the original gas was carbon monoxide. No evidence of water vapor was found showing hydrogen to be absent from the noncondensable gas. Hence, since methane is the only possible fixed gas at temperatures below the triple point of nitrogen, the traces of residual gas were assumed to be methane.

After the analysis of the noncondensable gas the liquid nitrogen trap was allowed to warm, and the gaseous products passed into the gas buret. Having shown by experiment that acetic anhydride is quantitatively trapped at -110°C , this second gaseous fraction was taken to be CO₂ and C₂ hydrocarbons. The total volume having been measured, CO₂ was absorbed over ascarite. Since no hydrogen had been found earlier, the probability of ethylene in the C₂ fraction was small, and, in general, the residual gas was taken to be ethane. Several explosion analyses, using a threefold excess of oxygen, which was found to give consistent results using pure ethane, justified the assumption.

In an attempt to characterize any liquid products from the reaction, five runs were made, each of one hour duration at 160°C and 24 mm initial pressure, and the liquid products, along with undecomposed acetic anhydride from all the runs, were collected in a cold-finger in dry ice and submitted to a mass-spectrometric analysis. A second series of runs of two-hour duration were made for the same purpose, liquid nitrogen being used instead of dry ice for the collection of products.

Some runs were made in an attempt to sensitize a decomposition of acetic anhydride using acetone. A quartz cell containing liquid acetic anhydride as a filter was placed between the lamp and the reaction vessel. Runs made using the anhydride vapor alone and acetone vapor alone showed appreciable decomposition of the acetone alone but no measurable decomposition of the anhydride alone. The difference in volatility of acetone and acetic anhydride made it

almost impossible to prepare mixtures containing a known small amount of acetone. Instead, samples of solutions of acetone in acetic anhydride, of known composition, were injected through the mercury seal, the samples being small enough to insure complete volatilization. In the analysis, the trap at -111°C was replaced with a petroleum ether slush at -150°C to separate acetone and carbon dioxide.

RESULTS

A typical series of runs of different duration at 80°C and 25 mm initial pressure are reported in Table I. The amounts of product are linear functions of the time, a result observed in all cases except at 60°C and 10 mm pressure, where carbon monoxide production exhibits an induction period as seen in Table II. Plots of these data extrapolate to the origin for ethane and carbon dioxide but the carbon monoxide data extrapolate to 23 min indicating that the carbon monoxide might be produced from a secondary species rather than directly from acetic anhydride. To observe any change in the ratios after appreciable photolysis, a run of fourteen-hours duration was also made at 60°C and 10-mm initial pressure.

In an attempt to identify any liquid products of the photolysis two samples were analyzed with the mass spectrograph.³ The first sample was collected from five, one-hour runs made at 160°C and 25 mm initial pressure, the products being trapped out with dry ice. The mass spectral range covered in the analysis did not extend beyond m/e values of 120. The only peak observed not attributable to acetic anhydride or acetic acid was at m/e of 57 and corresponded to an estimated 0.5 mole percent. A second sample, the products from five, two-hour runs under similar conditions but trapped out in liquid nitrogen, exhibited a more intense peak at the same value, 57, corresponding to an estimated one percent. It is significant that doubling the duration caused a doubling of the amount and indicates that the fragment represents a product of the reaction. A third sample, consisting of some of the acetic anhydride used for the photolysis to which 10% acetone had been added, was analyzed but showed no mass peak at 57. This precludes the possibility that the peak was due to any impurity in the starting material. Characteristic

TABLE II.

Temp. 60°C time (mm)	Initial pressure 10 mm		moles $\times 10^6$	
	CO	C ₂ H ₆	CO ₂	CH ₄
60	1.56	2.14	7.12	
70	2.00	2.45	7.80	
80	2.63	2.84	9.65	
90	2.72	3.16	10.5	
100	3.34	3.78	11.8	
840	29.5	28.8	60.7	3.65

³ The analyses were obtained through the courtesy of the M. W. Kellogg Company, New Jersey.

m/e values of biacetyl, acetyl-acetone, acetonyl-acetone, and methyl acetate were not observed in any of the spectra. The mass peak at 57 could correspond to the acetonyl radical and might suggest the presence of some more complex substance decomposing in the ion source.

The quantum yield of the photolysis was determined using acetone as an actinometer. Two twenty-minute runs at 160°C using acetone gave 0.138 cc carbon monoxide for an initial acetone pressure at 40 mm and 0.116 cc for an initial pressure of 36 mm. The latter gives 1.49×10^{17} molecules formed per minute; the former, 1.85×10^{17} . With unit quantum yield, these are also the numbers of quanta absorbed by the acetone per minute. Since the lamp did not emit monochromatic radiation, the calculation of the intensity of the incident radiation involved a summation over the several wavelengths present each with its spectral distribution factor and extinction coefficient. The incident intensity of the lamp estimated from the above data was found to be 4.3×10^{17} or 4.1×10^{17} quanta per minute, an average of 4.2×10^{17} .

For acetic anhydride the absorption data were taken from Ley and Arends.⁴ The anhydride absorbs at 2537 and at 2652 Å in the range studied giving the number of quanta absorbed per minute as 6.95×10^{16} . At 160°C and 25 mm the rate of production of carbon dioxide from acetic anhydride was $0.00565 \text{ cc min}^{-1}$ or 15.2×10^{16} molecules per minute. The quantum yield of carbon dioxide is thus 2.2. Table III summarizes the quantum yields.

In the two runs made with the acetone-acetic anhydride mixtures, owing to the slow rate of reaction, the quantities of gas for analysis were very small and the analytical results subject to large error. It is certain, however, from a qualitative point of view, that carbon dioxide was produced and in a quantity greater than carbon monoxide.

DISCUSSION

The results in Table III show that the initial rates of formation of the gaseous products are directly proportional to the initial pressure of the acetic anhydride. In the fourteen-hour run at 60°C, reported in Table II,

TABLE III. Quantum yields.

Temp. °C	Press. mm	CO	C ₂ H ₆	CO ₂
60	10	0.7 ^a	0.6	1.9
	80	0.8	0.8	1.9
120	20	0.8	0.8	2.0
	25	0.8	0.8	1.9
	10	1.2	1.1	2.2
	25	0.9	0.8	1.8
160	10	1.3	0.9	2.5
	25	1.1	0.8	2.2

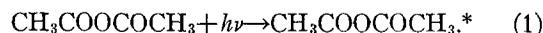
^a After the induction period.

⁴ H. Ley and B. Arends, *Z. physik. Chem.* **B17**, 177 (1932).

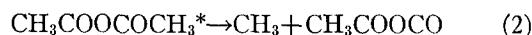
corresponding to about 42% decomposition, the volumes of CO and C₂H₆ are linear in time with the volumes produced after shorter irradiation, while the plot of the volumes of CO₂ falls quite appreciably. Nevertheless, the first order rate constant for CO₂ production calculated over the first 5% of reaction is 0.05 hr^{-1} while for the 42% reaction the value is 0.04 hr^{-1} . This agreement must indicate that the rate determining step in CO₂ production is approximately first order and the CO₂ may be taken as a measure of the amount of acetic anhydride decomposed. The validity of this assumption may be open to question, but it will be seen not to be inconsistent with the data. On the other hand, the continued steady production of CO and C₂H₆ even after 40% decomposition must mean that these are produced from species which have assumed a steady-state concentration.

The approximately first-order rate of the acetic anhydride photolysis is most easily accounted for on the basis of the weak absorption of the light. From the extinction coefficients at 2537 and 2652 Å it is calculated for the present experimental conditions that only 16% of the incident radiation is absorbed. Hence, the rate should be approximately proportional to the gas concentration. A first-order rate will, however, be an upper limit and actually on this account alone the order of the reaction should be less than unity.

The primary process may then be written as producing an excited molecule:



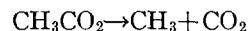
Whether this molecule may be deactivated by collision with other molecules, or lose energy by fluorescence cannot be ascertained from the present work. The fate of the excited molecule presents two possibilities for consideration:



or



There is very little direct information concerning the acetate radical. Rice⁵ estimated the energy of activation of the reaction:



to be between 40 and 70 kcal which agrees with Burton's⁶ interpretation of the vapor phase photolysis of acetic acid. On this basis the acetate radical should be relatively stable and the CO₂/CO ratio should be less than unity and certainly not much greater than one at temperatures around 100°C. Experimentally it is seen that the CO₂/CO ratio remains about two regardless of temperature or pressure indicating that CO₂ is produced more easily than CO which would not be expected if the acetate radical were the major source of CO₂. Further-

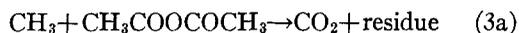
⁵ F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals* (Johns Hopkins Press, Baltimore, Maryland, 1935), p. 187.

⁶ M. Burton, *J. Am. Chem. Soc.* **58**, 692, 1645 (1936).

more, owing to the acetate stability, a reaction with methyl to produce methyl acetate would be expected to occur without difficulty, whereas none was found in the mass spectrographic analyses. Finally, the rate of formation of CO_2 has a negligible temperature coefficient, quite inconsistent with its production from acetate radicals requiring 40 to 70 kcal for decomposition. Reaction (2') is, therefore, not consistent with the experimental observations.

There remains the alternative reaction (2). To produce CO_2 in the amounts found, the CH_3COOCO radical must decompose readily leaving an acetyl radical. From the work of Herr and Noyes⁷ on acetone photolysis, the acetyl radical appears to decompose readily at temperatures above 100°C as shown by the unit quantum yield for CO but at lower temperatures becomes stabilized as biacetyl with a corresponding deficiency in CO production. The results found in the 60°C run are very similar and could therefore be similarly accounted for. On the other hand, Pitts and Blacet⁸ have interpreted their studies of acetone photolysis in presence of iodine to indicate that acetyl radicals are stable up to at least 175°C in presence of small concentrations of free radicals. In presenting an alternative explanation Nicholson⁹ observes that it is "meaningless to compare the stabilities of free radicals in different systems unless all the rate constants of the reactions in which the radicals disappear are known." There is at least one difference between the acetyl radicals produced in the acetone and the acetic anhydride systems. The activated anhydride molecule has absorbed about 110 kcal/mole. If 80 kcal are used in breaking the C—C bond, 30 kcal remain to be divided between the two fragments and if neither is electronically excited, the CH_3COOCO radical would get no more than 5 kcal/mole. The subsequent splitting out of CO_2 should leave a very "cold" acetyl radical. In acetone photolysis the acetyl radical initially formed is much more energetic. In addition, the reactivity of acetyl radicals in an atmosphere of acetic anhydride need not necessarily be identical with that in acetone.

The quantum yield of two found for CO_2 was essentially constant over the temperature range covered. The slight increase with temperature is not inconsistent with an effect of temperature on the extinction coefficients of acetic anhydride. The quantum yield of two requires that a second molecule of the anhydride decompose to yield a molecule of CO_2 subsequently to the initial split. Two reactions appear possible:



⁷ D. S. Herr and W. A. Noyes, *J. Am. Chem. Soc.* **62**, 2052 (1940).

⁸ J. N. Pitts and F. E. Blacet, *J. Am. Chem. Soc.* **74**, 6155 (1952).

⁹ A. J. C. Nicholson, *J. Chem. Phys.* **20**, 1811 (1952).

The early production of C_2H_6 , observed in all the runs made, probably occurs by combination of the methyl radicals formed in reaction (2). In the 60°C run, however, the amount of C_2H_6 produced early in the reaction is only about one-third and not one-half of the CO_2 produced. There is thus a deficiency in the methyl radicals. Later in the reaction at 60°C the $\text{CO}/\text{C}_2\text{H}_6$ ratio approaches two just as at higher temperatures. This would not seem consistent with a removal of acetyl radicals as biacetyl at 60°C . Reactions (3a) and (3b) can thus account for both the methyl radical deficiency as ethane and for the removal of acetyl radicals. The possibility of either of these reactions was at least qualitatively established by the runs made with the anhydride-acetone mixtures where methyl or acetyl radicals from acetone photolysis produced a decomposition of the anhydride as evidenced by the production of CO_2 .

The reaction of an acetyl or a methyl radical with anhydride presents a problem in accounting for the observed over-all order, approximately the first. In the absence of its decomposition the acetyl radical concentration should be proportional to the light absorbed, that is, approximately proportional to the anhydride concentration. The reaction of acetyl with anhydride would thus be approximately second order. The total rate of disappearance of acetic anhydride as measured by CO_2 production would be $k_2[A] + k_3[A]^2$, where A stands for the anhydride, with an over-all order between one and two. The maximum dependence of the concentration of methyl radicals, produced by reaction (2) and removed by recombination, on the concentration of acetic anhydride would be the square root and reaction (3a) would be three-halves order. It has already been pointed out, however, that the first-order dependence of reaction (2) is an upper limit owing to the approximation for weak absorption and hence the order approximately first, found here is not inconsistent with either reactions (3a) or (3b).

The identification of the residue of reactions (3) could not be made. A material balance, based on the assumption that CO_2 measures the acetic anhydride decomposed, carried out on the gaseous products indicates that the over-all residue unaccounted for has the empirical formula $\text{C}_3\text{H}_5\text{O}$. The mass-spectrographic analysis of the liquid produced a fragment of mass-to-charge ratio of 57 which could have the empirical formula $\text{C}_3\text{H}_5\text{O}$. Since the characteristic mass peaks of biacetyl, acetone, acetyl acetone, acetyl acetone, and methyl acetate were not observed in any of the mass spectra, it was concluded that these substances were not present to an extent greater than 0.5 mole percent. The unidentified 57 peak was present in an amount which would lead to a material balance. Damon and Daniels¹¹ found that a trace of water catalytically

¹¹ G. H. Damon and F. Daniels, *J. Am. Chem. Soc.* **55**, 2363 (1933).

produced a photochemical condensation of acetone, although the product was not completely identified. It could be surmised that the acetyl radical could induce some condensation or polymerization reaction with the ejection of a molecule of CO_2 from the condensate which in the mass spectrograph produces the fragment of mass 57.

At 160°C , and probably more so at higher temperatures, some methane is produced. This undoubtedly results from a hydrogen abstraction reaction of methyl radicals with acetic anhydride. The fate of the radical produced may only be speculated, but presumably it either breaks down or enters into a recombination reaction.

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Study of Electrokinetic Effects Using Sinusoidal Pressure and Voltage*

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The electrokinetic effects streaming potential, streaming current, and electro-osmotic pressure were studied by applying and measuring sinusoidal variations of hydrodynamic pressure and electrical voltage. Phenomenological relations between the effects were investigated, and an improved experimental method for measuring the electrokinetic coefficients, hence the zeta potential, was used. Saxen's law was verified within 6% at frequencies of 20, 100, and 200 cycles per second. The systems studied were restricted to glass-water and glass-salt solutions. The advantages and disadvantages of using sinusoidally varying quantities for electrokinetic measurements are discussed.

IN recent years the streaming potential has been applied in various types of pressure transducers.^{1,2} Packard³ has developed a theoretical expression for the variation of the streaming potential with frequency, and has made experimental measurements of the sinusoidal potential developed across capillaries upon application of a sinusoidal pressure. The phenomenon of electro-osmosis has been investigated extensively using a constant applied voltage. To the author's knowledge it has never been studied quantitatively before using an applied electrical voltage which varies sinusoidally with time. The advantage of using the alternating voltage to measure the magnitude of the electrokinetic potential is, of course, the possibility of alleviating difficulties which arise at the electrodes.

PHENOMENOLOGY OF THE ELECTROKINETIC EFFECTS

The electrokinetic effects which are considered here are of a class of irreversible processes which have been treated in theory.⁴ The phenomenological relations between the electrokinetic effects have also been thoroughly discussed in the literature.^{5,6}

* This paper is part of a dissertation submitted to the Graduate School of the University of Texas in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work was partially supported by a grant from Research Corporation.

† Present address: Houston Research Center, Humble Oil and Refining Company, Houston, Texas.

¹ M. Williams, *Rev. Sci. Instr.* **19**, 640 (1948).

² E. V. Hardway, *Instruments* **26**, 1186 (1953).

³ R. G. Packard, *J. Chem. Phys.* **21**, 303 (1953).

⁴ S. R. De Groot, *Thermodynamics of Irreversible Processes* (North Holland Publishing Company, Amsterdam, 1951).

⁵ J. Th. G. Overbeek, *J. Colloid Sci.* **8**, 421 (1953).

⁶ P. B. Lorenz, *J. Phys. Chem.* **56**, 775 (1952).

The so-called phenomenological equations describing the electrokinetic effects are

$$I = L_{11}E + L_{12}P, \quad (1)$$

$$V = L_{21}E + L_{22}P. \quad (2)$$

I , electric current through the system, is taken as positive when flow is from side 1 to side 2. E , electric potential across the system, is taken as positive when side 1 is positive with respect to side 2. Similar convention is used for the hydrodynamic quantities volume flow, V , and pressure, P . The coefficients (L_{ij}) are called the phenomenological coefficients. It can be seen that L_{11} and L_{22} are the ordinary electrical and hydrodynamic conductance coefficients. L_{12} and L_{21} are the electrokinetic coefficients.

From Eqs. (1) and (2),

$$L_{12} = -L_{11} \frac{E_s}{P} + \frac{I_s}{P} \quad (3)$$

$$L_{21} = -L_{22} \frac{P_{e0}}{E} + \frac{V_{e0}}{E}. \quad (4)$$

The subscripts have been added to designate the streaming potential and streaming current, E_s and I_s , and the electro-osmotic pressure and volume flow, P_{e0} and V_{e0} .

Note that if the coefficients are positive the equations imply positive charge transport in the liquid from application of a positive pressure. If an excess of negative charges exists in the flowing liquid then the coefficients L_{12} and L_{21} are negative. In any case, the