

equation it appears that, initially, the surface tension of the solid, S_{sa} , decreases more in passing from one derivative to the next higher one than does the interfacial tension solid-liquid, S_{sl} , but that beyond the maximum point the reverse is true. This explanation agrees with other facts, *i.e.*, that the tensile strength and density (to a first approximation proportional to S_{sa}) decrease throughout quite linearly with increasing side chain length, whereas solubility and swelling effects (inversely related to S_{sl}) become much more pronounced starting with the tributyrate.

Hysteresis Effects.—As can be seen from the tables differences between the advancing and receding angles, for the liquid-solid combinations which give finite angles, ranged from 8° to over 50° . In each case the amount of the hysteresis appears to be characteristic of the derivative and of the mode of formation of the surfaces.

The organic liquids gave hysteresis effects which on some solids exceeded those given by water. There is some indication, at least for methylene iodide, that the effects with organic liquids are the inverse of those with water. As shown in Fig. 1 the hysteresis with methylene iodide becomes a

maximum at the tripropionate, whereas that with water is a minimum.

That the magnitude of the hysteresis effect is dependent upon the mode of formation of the surface is clearly shown in Table II upon comparing $\Delta\theta$ values for the opposite sides of foils. The higher values are for the "glass" sides where the average value is nearly double that found for the "air" sides. As brought out in the last two columns of the table these differences in hysteresis are for the most part the result of differences in the receding angles on the opposite sides. The majority of the receding angles are around 20° lower on the "glass" sides than on the "air" sides while the advancing angles differ little or none on the two sides. Ethyl cellulose furnishes the exception to the above generalization. With it the contact angles and hysteresis were the same for the two sides of the foil. A possible explanation for the smaller receding angle on the "glass" side is that molecular orientation occurred in the surface of the cellulose derivative against the hydrophilic glass which caused this surface of the polymer to become more hydrophilic.

ANN ARBOR, MICHIGAN

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

Photochemical Studies. XLV. The Reactions of Methyl and Acetyl Radicals with Oxygen¹

BY FRANK B. MARCOTTE AND W. ALBERT NOYES, JR.

Acetyl radicals apparently do not yield either carbon monoxide or carbon dioxide upon reaction with oxygen although it appears that two molecules of oxygen are consumed per radical. It is possible to obtain a rough estimate for the activation energy of the reaction $\text{CH}_3\text{CO} = \text{CH}_3 + \text{CO}$ if it is assumed that the activation energy for reaction of acetyl radical with oxygen is very small. Previous work has been extended to give some further information about the formyl radical.

Some results obtained during exposure of mixtures of acetone and oxygen, the latter at quite low pressures, have already been presented.² Due to the fact that the quantum yields of oxygen disappearance and of the sum of carbon monoxide and carbon dioxide formation were in general approximately small whole numbers, it was possible to present a relatively simple mechanism which accounted for most of the facts. Not many, if any, of the steps in this mechanism could be proved conclusively although no alternative mechanism of equal plausibility could be suggested. The present work is a continuation of that already reported and helps to elucidate certain of the steps.³

Experimental

The experimental procedure used in this investigation has been described adequately.³ Analyses were performed for methane, carbon monoxide, ethane and carbon dioxide, and values were also obtained for the amount of oxygen

consumed during the course of the reaction. Methane, carbon monoxide and oxygen were separated from all other products as well as from the acetone by condensation with liquid nitrogen. Since ethane is not produced when oxygen is present, it proved unnecessary to use supercooled liquid nitrogen. The oxygen, carbon monoxide and methane were heated in a furnace containing a mixture of copper and copper oxide. The oxygen is removed as copper oxide, the carbon monoxide is oxidized to carbon dioxide, and the methane is not affected by this procedure.

Since the method of competing reactions was used, low pressures of oxygen were essential. In order to avoid its depletion, small amounts of oxygen were added from time to time by means of a small Toepler pump. The gases were circulated by a small glass propeller.

Quantum yields are based on a value of unity for the quantum yield of carbon monoxide formation in pure acetone vapor at temperatures between 120 and 225° .^{4,5}

Results

The important matters in the present discussion are the details of the variation of the yields of carbon monoxide, carbon dioxide, and oxygen disappearance as a function of oxygen pressure over the temperature range, 120 to 225° . Figure 1 shows carbon monoxide yield as a function of oxygen pressure at five different temperatures whereas Fig. 2 shows similar data for the carbon dioxide yield. Figure 3 shows the variation of methane yield.

It is evident that the yield of carbon dioxide passes through a maximum as a function of oxygen pressure at the lower temperatures in this temperature range. It may do so

(1) This work was supported in part by Contract N6onr-241, Task I, with the Office of Naval Research, United States Navy.

(2) F. B. Marcotte and W. A. Noyes, Jr., *Discussions Faraday Soc.*, No. 10 (1951).

(3) For detailed tables of data pertaining to this work order Document 3366 from American Documentation Institute, 1719 N Street N. W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1" high on standard 35 mm. motion picture film) or \$1.05 for photocopies (8" x 8") readable without optical aid.

(4) J. A. Leermakers, *This Journal*, **56**, 1899 (1934).

(5) D. S. Herr and W. A. Noyes, Jr., *ibid.*, **68**, 2052 (1940).

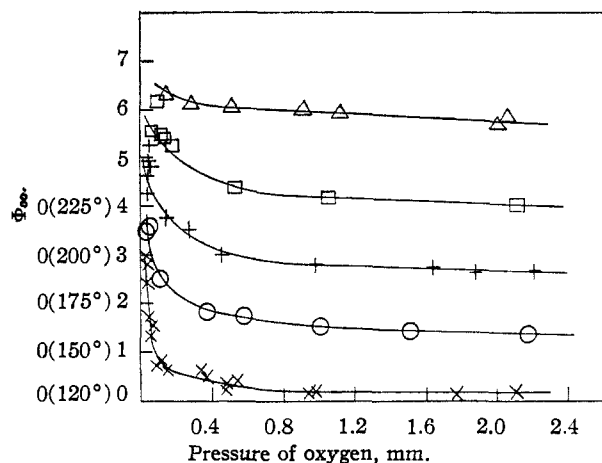


Fig. 1.—Variation of Φ_{aO} with oxygen pressure at several temperatures: $I_a = 10^{12}$ quanta/cc./sec.; acetone pressure, 131.3 mm. The origin for each curve is shown on the left margin. Each origin lies one unit above the next lower: \times , 120°; \circ , 150°; $+$, 175°; \square , 200°; Δ , 225°.

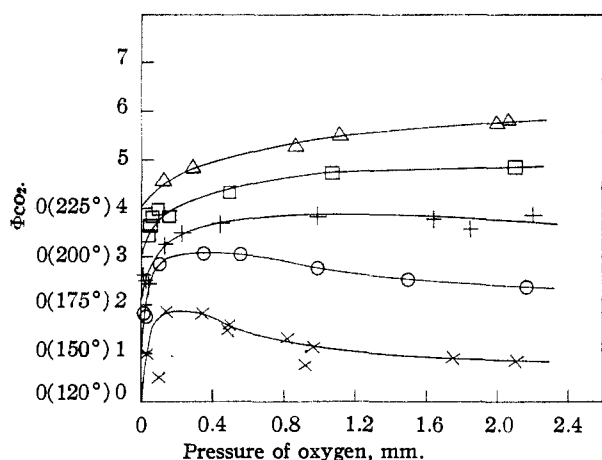


Fig. 2.—Variation of Φ_{aO} with oxygen pressure at several temperatures: $I_a = 10^{12}$ quanta/cc./sec.; acetone pressure, 131.3 mm. The origin for each curve is shown on the left margin. Each origin lies one unit above the next lower: \times , 120°; \circ , 150°; $+$, 175°; \square , 200°; Δ , 225°.

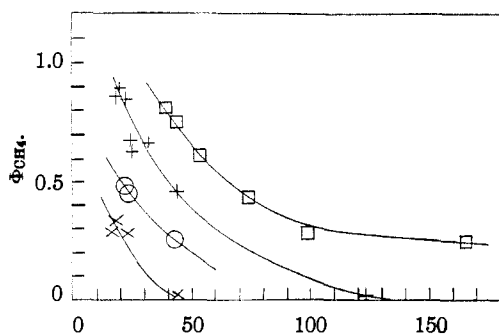


Fig. 3.—Dependence of Φ_{CH_4} on oxygen pressure at several temperatures: $I_a = 10^{12}$ quanta/cc./sec.; pressure of acetone, 131.3 mm.; \times , 120°; \circ , 150°; $+$, 175°; \square , 200°.

at all temperatures, but at higher temperatures it is not feasible to operate at sufficiently high oxygen pressures to make this apparent, and the yields approach constancy asymptotically.

The carbon monoxide yield must also pass through a

maximum since in the absence of oxygen the yield is unity. However, at most of the temperatures it is not possible to operate at sufficiently low pressures to show the existence of this maximum. Indeed the scatter in the results is such that with the sharp maximum found it is hard to tell which side of the peak a given point lies. Suffice to say that at an acetone pressure of about 130 mm. the maximum value of 3 for Φ_{CO} is obtained at an oxygen pressure of 0.02 mm. or less and the course of the curve below this pressure has not been established, although the value must be unity at zero oxygen pressure.

The value of Φ_{O_2} , the quantum yield of oxygen disappearance, differs but little from 4 under nearly all conditions from 120 to 225°, although there may be a slight trend with oxygen pressure as shown in Fig. 4.

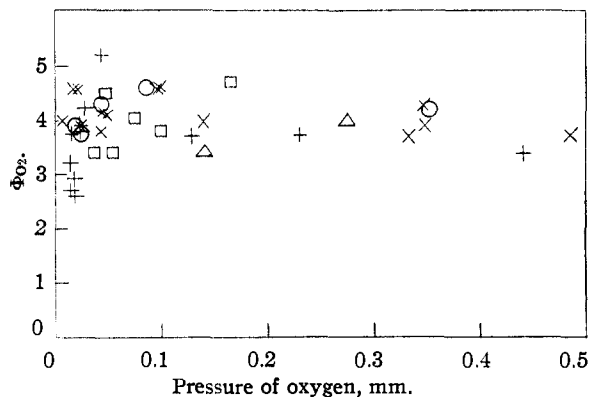


Fig. 4.—Dependence of Φ_{O_2} on oxygen pressure at several temperatures: $I_a = 10^{12}$ quanta/cc./sec.; pressure of acetone, 131.3 mm.; \times , 120°; \circ , 150°; $+$, 175°; \square , 200°; Δ , 225°.

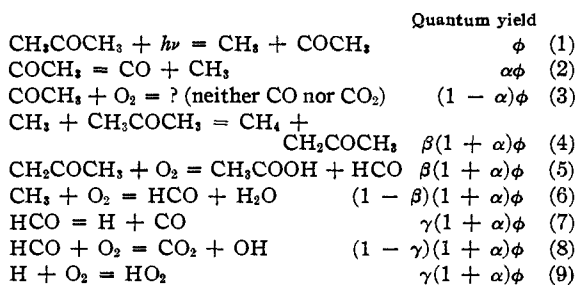
The runs were nearly all performed at constant incident light intensity. Such data as have been obtained show no variation beyond experimental error with light intensity although the data are not extensive enough to permit a definite conclusion as to what the effect of light intensity might be if it were varied over wide limits.

The effect of acetone pressure has not been studied extensively. There is, perhaps, a slight tendency for Φ_{CO} to increase and for Φ_{CO_2} to decrease as the acetone pressure increases, but Φ_{O_2} is essentially constant.

The quantum yield of ethane formation was always zero even at the lowest oxygen pressure at all temperatures. The yield of methane decreases as the oxygen pressure increases as would be expected.

Discussion of Results

It seems best to repeat the mechanism already presented and to discuss the present results in terms of it. The products of reaction (3) are now indicated as uncertain, and in this respect this presentation differs from that given earlier.



The definitions of symbols are obvious but will be stated: ϕ = primary quantum yield; α = fraction of $COCH_3$ radicals which dissociate; β = fraction of CH_3 radicals which form methane; γ = fraction of HCO radicals which dissociate.

The value of ϕ deserves consideration. In the absence of foreign gases ϕ is almost certainly nearly unity.^{4,5} In the presence of iodine at 3130 Å. it is well below unity⁶ and with several millimeters iodine pressure it may be as low as 0.17 at 100°. Thus iodine must have the effect of deactivating acetone molecules which would otherwise dissociate.⁷ The effect of oxygen on the primary quantum yield cannot be stated with certainty, but it is probably negligible as based on the following facts: (1) The maximum value of Φ_{CO} indicates quite strongly that one CO is formed from dissociation of the acetyl radical and one for each methyl radical which reacts with oxygen at low pressures. Thus low pressures of oxygen almost certainly do not lower the primary quantum yield.

(2) An increase in temperature causes (a) a disappearance of the structure of the acetone fluorescence, an effect also produced by oxygen⁸; (b) a decrease of the quenching of the fluorescence by oxygen. Thus at temperatures such that the primary quantum yield must be very close to unity,^{4,5} the effect of oxygen on the fluorescence is small.

(3) The "activation energy" for the dissociation of the initially formed "activated molecules" seems to be appreciable⁹ so that at the temperatures of these experiments their rate of dissociation should be high even though it may not be at room temperature. The rate should be at least 25 times as great at 200° as at 25°. Thus we believe on the basis of good evidence but without complete proof that the quantum yield of the primary process is close to unity in all experiments herein discussed.

The value of α may next be discussed. If $\phi = 1$, α cannot exceed the value of Φ_{CO} and it will have this value only if CO is formed only by reaction (2). An inspection of Fig. 2 shows that Φ_{CO} falls well below unity at sufficient oxygen pressures at temperatures of 120–175°. However, one may deduce from the mechanism² that $\Phi_{\text{O}_2} = (3 + \alpha)\phi$ and hence a maximum value of 4ϕ and a minimum value of 3ϕ would be obtained. Since $\Phi_{\text{O}_2} \sim 4$ even when $\Phi_{\text{CO}} < 1$, this equation must not be correct. One must assume, therefore, that equation (3) is not correct and that a sequence of events must be started which causes two molecules of oxygen to disappear. With this assumption

$$\Phi_{\text{O}_2} = 4\phi \quad (10)$$

in satisfactory agreement with the facts.

It is now possible to obtain information about the acetyl radical. One may write

$$\Phi_{\text{CO}} + \Phi_{\text{CO}_2} = (1 + 2\alpha) \quad (11)$$

if $\phi = 1$. Hence one may write

$$(\text{O}_2) \times \frac{\Phi_{\text{CO}} + \Phi_{\text{CO}_2} - 1}{(3 - \Phi_{\text{CO}} - \Phi_{\text{CO}_2})} = \frac{k_2}{k_3} \quad (12)$$

Thus one can obtain k_2/k_3 if the assumptions are valid and from a plot of $\log(k_2/k_3)$ vs. $1/T$ one

(6) F. E. Blacet and J. N. Pitts, Jr., private communication. See also S. W. Benson and G. S. Forbes, *THIS JOURNAL*, **65**, 1399 (1943); E. Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

(7) W. A. Noyes, Jr., *J. Phys. Colloid Chem.*, **55**, 925 (1951).

(8) G. W. Luckey and W. A. Noyes, Jr., *J. Chem. Phys.*, **19**, 227 (1951).

(9) W. A. Noyes, Jr., and L. M. Dorfman, *ibid.*, **16**, 738 (1948).

can obtain the activation energy difference $E_2 - E_3$. The nature of equation (12) is such that a high accuracy would not be expected, but $E_2 - E_3 \sim 16$ kcal. with an estimated uncertainty of about 2 kcal. At temperatures over 175°, $3 - \Phi_{\text{CO}} - \Phi_{\text{CO}_2}$ is so nearly zero as to render calculations by equation (12) meaningless. The activation energy of (3) is unknown but is probably small in common with reactions of other radicals with oxygen. Hence we may write tentatively $E_2 = 16 \pm 2$ kcal.

The complete equation for Φ_{CO} , as a function of oxygen pressure may be derived from the mechanism by the assumption of the steady state and is

$$\Phi_{\text{CO}_2} = \frac{(k_8(\text{O}_2)\phi(3k_2 + k_3(\text{O}_2)))}{(k_7 + k_8(\text{O}_2))(2k_2 + k_3(\text{O}_2))} \quad (13)$$

This equation is of the right form but is not useful for deriving constants from the data. An equation for Φ_{CO} as a function of oxygen pressure will not show a maximum unless one introduces the reaction $\text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_6$ or some other radical combination reaction which causes methyl radicals to disappear.

If $\alpha = 1$ and $\phi = 1$, *i.e.*, if the oxygen pressure is below that for the maximum yield of carbon dioxide and if the temperature is toward the upper part of the range studied, one finds

$$1/\Phi_{\text{CO}_2} = k_7/2k_8(\text{O}_2) + 1/2 \quad (14)$$

Plots of equation (14) give reasonably good straight lines at 175, 200 and 225° with an intercept of about 0.5. The slope may be used to calculate k_7/k_8 . The numerical values calculated in the above manner agree well but not exactly with those calculated by the method already given.² Nevertheless the trend with temperature is the same and differences may be ascribed to scatter in the data. From a plot of $\log(k_7/k_8)$ vs. $1/T$ one obtains $E_7 - E_8 \sim 14$ kcal. with an estimated uncertainty of about 1 kcal. If $E_8 = 0$, as seems probable, one obtains $E_7 \sim 14$ kcal. This value may be compared with 14 kcal. obtained by Blacet and Calvert¹⁰ and 13.4 kcal. obtained by Calvert and Steacie.¹¹

A word may be said about the natures of reactions (3), (5), (6) and (8). They probably all proceed by the initial step $\text{R} + \text{O}_2 = \text{RO}_2$. At high radical concentrations peroxides may result from $\text{RO}_2 + \text{R}' = \text{RO}_2\text{R}'$, but under the conditions of these experiments rearrangements leading to dissociation seem to be rapid compared to radical capture. Activation energies for these rearrangements cannot be estimated but they could be appreciable and still permit them to compete with radical capture due to the low concentrations of radicals in these experiments. Another possibility often suggested is $\text{RO}_2 + \text{R}'\text{H} = \text{RO}_2\text{H} + \text{R}'$,¹² but this reaction should have an appreciable activation energy and does not seem to be important under conditions of these experiments.

A word may also be said about pre-exponential factors for the dissociations of formyl and acetyl

(10) F. E. Blacet and J. G. Calvert, *THIS JOURNAL*, **73**, 666 (1951).

(11) J. G. Calvert and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 181 (1951).

(12) See A. D. Walsh, *Trans. Faraday Soc.*, **42**, 269 (1946); **48**, 297, 305 (1947).

radicals. It has already been shown² that reaction (6) has a low steric factor, *i.e.*, about two collisions in 10^4 lead to reaction in spite of the low activation energy. If this same factor is assumed for (8), pre-exponential term for (7) is very low, of the order of 10^9 sec.⁻¹ instead of the usual value of about 10^{13} sec.⁻¹ for many unimolecular reactions. However, HCO has few vibrational degrees of freedom and quite possibly the dissociation rate will depend markedly on total pressure. If this is true, the constant for (7) will be complex, and statements concerning activation energy and steric factors must be made with care.

The same type of reasoning when applied to reaction (2) shows the pre-exponential factor to be about 10^{12} sec.⁻¹. Thus this radical with its larger number of degrees of freedom may decompose by a more nearly unimolecular process. It is safe to say that CH_3CO radicals decompose more rapidly than HCO radicals at a given oxygen pressure in spite of their higher activation energy for decomposition.

One further uncertainty exists concerning the mechanism as postulated, and this concerns the fates of the OH and HO_2 radicals. If either of these abstracts hydrogen or regenerates oxygen directly or indirectly, some uncertainties in the interpretation would exist. On the other hand, at the temperatures covered by these experiments a chain reaction has not been initiated, and for this reason it seems probable either that these radicals disappear mainly by combination with each other, or that eventually they react with the mercury vapor in the system. In this respect acetone-oxygen mixtures behave very differently from diethyl ketone-oxygen mixtures which will be discussed in a later paper.¹³ Any hydrogen abstraction by either OH or HO_2 would presumably lead to the same acetyl radical as results from methane formation and consequently could lead to a chain reaction. Some evidence that this type of thing occurs at 250° and higher has been noted.

(13) Work being performed by Dr. A. Finkelstein in this Laboratory.
ROCHESTER, NEW YORK RECEIVED JULY 5, 1951

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

A Study of Interactions between Dipole Molecules in Benzene Solution by a Cryoscopic Method¹

BY BERNARD C. BARTON,² DAVID A. ROTHROCK, JR., AND CHARLES A. KRAUS

The interaction between dipolar molecules in benzene solution has been investigated by the cryoscopic method. The freezing point depression of seventeen dipolar substances has been measured as a function of concentration. In addition, the freezing point depression has been determined for equimolar mixtures of several pairs of dipolar molecules. If $r = \Delta T/\Delta T_0$ is the ratio of the depression for a given solution to that of an ideal solution then, in general, the results conform to the linear relation, $r = 1 - b'm$, where m is the formal concentration and b' is a constant which serves as a measure of the degree of interaction. With equimolar mixtures of two different dipolar molecules, measurable interaction occurs between molecules of different species.

I. Introduction

In an ideal system, the freezing point depression, ΔT_0 , of a dilute solution is directly proportional to its concentration, or

$$\Delta T_0 = am \quad (1)$$

where m is the formal concentration and a is the freezing point constant. In the case of a solute consisting of polar molecules, the freezing point depression, ΔT , is usually less than ΔT_0 , the depression for an ideal solution at the same concentrations. As a first approximation we might express the result by means of a quadratic equation of the form

$$\Delta T = am - bm^2 \quad (2)$$

where b is a constant which will be the larger the greater the interaction between the solute molecules. In practice, it is more convenient to examine values of the ratio $r = \Delta T/\Delta T_0$ rather than of ΔT , itself. Expressed in this manner, equation (2) becomes

$$r = \Delta T/\Delta T_0 = 1 - b'm \quad (3)$$

where the constant b' is the slope of the curve relat-

ing r with m and serves as a measure of the interaction between the dipole molecules.

There are numerous data in the literature which show that the freezing point depression for solutions of dipolar molecules is less than that of corresponding solutions of an ideal substance.⁸ However, the available data, for the most part, relate to relatively concentrated solutions and their precision is not sufficiently high to permit of determining how closely they conform to equation (3). Furthermore, it seemed of interest to examine how the deviations from ideal systems may be dependent upon the dipole moments of the dissolved molecules. Accordingly, we have measured the freezing point depression of some seventeen polar substances in benzene, chiefly in the concentration range of 0.01–0.1 m . In addition, we have measured the freezing point depression of solutions of several sets of two different dipolar substances for the purpose of determining the interaction between molecules of different species.

The data for all substances and their equimolar mixtures here reported follow relation (3). As Lassette⁸ has shown, the linear dependence of the ratio M/M_0 (or r) on m may be accounted for satisfactorily by assuming successive association

(1) This paper is based on a portion of a thesis presented by Bernard C. Barton in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1939.

(2) University Fellow in Brown University, 1936–1939, *inc.*

(3) E. N. Lassette, *Chem. Revs.*, **20**, 259 (1937); *THIS JOURNAL*, **69**, 1383 (1937).