

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C. 20234]

Triplet-State Energy Transfer from Acetone to Aliphatic Aldehydes in the Gas Phase

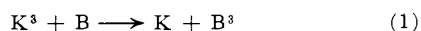
BY R. E. REBBERT AND P. AUSLOOS

RECEIVED JUNE 11, 1964

The effect of relatively small concentrations of aldehyde on the gas-phase photolysis of acetone has been investigated. It is shown that aldehydes quench the phosphorescence emitted by acetone at 3130 Å. but do not affect its fluorescence. The relative quenching efficiency of 2-butenal, butyraldehyde, propionaldehyde, and acetaldehyde is 100:2.7:1.9:0.95. On the basis of the experimental observations, it is suggested that an acetone molecule can transfer its triplet-state energy to form a triplet excited aldehyde molecule. It is shown that the electronically excited aldehyde molecule formed in such an energy-transfer process shows the same modes of decomposition as in the direct photolysis. The energy-transfer process does not occur in the presence of oxygen and decreases in probability with an increase in temperature.

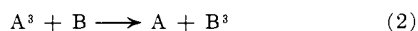
Introduction

Investigations carried out at the University of Rochester have shown that the addition of biacetyl to simple aliphatic ketones inhibits their decomposition in various degrees, the quenching being the most pronounced in the case of acetone.¹⁻³ It was also demonstrated that the phosphorescence emitted by the latter compound is readily quenched by biacetyl while the fluorescence remained relatively unaffected. These observations were adequately accounted for by the energy-transfer process



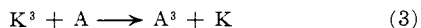
That a triplet excited biacetyl molecule is indeed formed in this process was proven⁴ by the observation of a strong emission coinciding with the phosphorescence of biacetyl as seen in the direct photolysis of this compound.

Recently, it has been reported⁵ that a similar energy-transfer process can take place between an aliphatic aldehyde molecule and biacetyl.



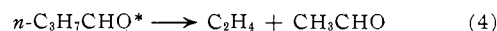
Because most aldehydes do not phosphoresce, the occurrence of the latter process could only be based on the appearance of the phosphorescent emission from biacetyl and the corresponding quenching of the photochemical decomposition of the aldehyde. The fact that, in this study, the fluorescence emitted by the aldehyde remained unaffected by the addition of biacetyl demonstrated that the energy-transfer process did not involve an aldehyde molecule excited to the upper singlet state.

The present investigation was undertaken in order to determine if the transfer of triplet-state energy can also take place between a triplet excited acetone molecule and an aldehyde.



The occurrence of this process will be examined by following (a) the quenching of the phosphorescence emitted from acetone by a number of aldehydes and (b) the decomposition of the excited aldehyde molecule formed in the energy process. The second approach will be exclusively concerned with *n*-butyraldehyde, mainly because it is well established that an electronically excited *n*-butyraldehyde can eliminate ethylene

in a rearrangement process⁶



At low temperatures, ethylene will not be formed by secondary free-radical reactions so that a determination of the quantum yield of ethylene provides a convenient way to follow the probability of process 4 under various conditions.

Experimental

Acetone (Spectro Grade), acetaldehyde, propionaldehyde, *n*-butyraldehyde, and 2-butenal were obtained from Eastman Kodak Company. The *n*-butyraldehyde was purified on a spinning-band distillation column. All compounds were thoroughly degassed and stored at -80° . The oxygen was assayed reagent grade and was obtained from the Air Reduction Company.

The fluorescent and phosphorescent measurements were carried out in a high-quality quartz fluorescent T-shaped cell, 56 mm. long and 28 mm. in diameter. The gases were continuously circulated through the cell with a glass circulating pump. The total volume of the system was about 500 cc. The light emitted by the gas at right angles passed through a quartz window and a Corning 3850 filter to a 1P28 photomultiplier tube.

The light source was an Osram-200 lamp, used in conjunction with a Bausch and Lomb grating monochromator of 250-mm. focal length, with entrance and exit slits 0.5 mm. wide. The relative fluorescent yields, reported in this paper, were calculated from the equation $Q_{rel} = (F - F_0)/I_0 - I_t$, where F is the galvanometer deflection for the emitted light with the gas in the cell, F_0 is the deflection for the emitted light with the cell empty, I_0 is the intensity of the light recorded with the cell empty, and I_t is the intensity transmitted with gas in the cell. Because the relative emission yields reported in this study were obtained at a constant concentration of the ketone, no correction needed to be applied for the fact that the intensity is somewhat lower in the center of the cell than close to the front window. The pressure of the additive was always small so that, in all cases, more than 95% of the total absorbed light was absorbed by acetone. Exposure of the mixtures which were investigated was kept to a few seconds in order to prevent the accumulation of biacetyl as a significant product.

The photolysis experiments were carried out in a separate system which has been described in an earlier study.⁷ The light source was an Hanovia SH-100 lamp used in combination with a Corning 0-54 filter which transmits wavelengths at 3130 Å. and above. The quantum yields were determined by photolyzing acetone at 140° . If, at this temperature, one assumes the quantum yield of CO to be unity,⁸ then 4.87×10^{12} quanta are absorbed per cc. of acetone per second at an acetone pressure of 10.0 cm.

After photolysis, the reaction products were separated by low-temperature distillation from -210 to -150° . The different fractions were further analyzed by mass spectrometry. Conversions were kept low enough so that not more than 5% of the added aldehyde was decomposed.

(1) J. Hecklen and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **81**, 3858 (1959).
 (2) D. S. Weir, *ibid.*, **83**, 2629 (1961).
 (3) J. L. Michael and W. A. Noyes, Jr., *ibid.*, **85**, 1027 (1963).
 (4) H. Okabe and W. A. Noyes, Jr., *ibid.*, **79**, 801 (1957).
 (5) R. P. Borkowski and P. Ausloos, *ibid.*, **84**, 4044 (1962).

(6) F. E. Blacet and J. G. Calvert, *ibid.*, **73**, 667 (1951).
 (7) R. P. Borkowski and P. Ausloos, *J. Phys. Chem.*, **65**, 2257 (1961).
 (8) D. S. Herr and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **62**, 2052 (1940).

Results

1. **Quenching of the Phosphorescence Emitted by Acetone.**—Figure 1 gives a typical plot showing the quenching of the total observed emission from acetone as a function of added *n*-butyraldehyde. A similar

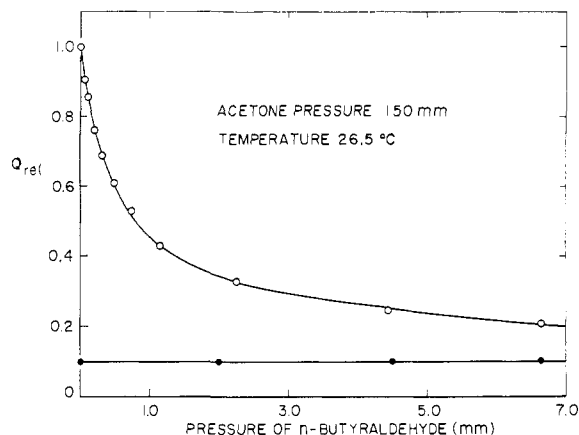


Fig. 1.—Relative emission yield as a function of pressure of *n*-butyraldehyde: O, total emission; ●, emission in the presence of oxygen.

quenching of the emission is also observed for acetaldehyde, propionaldehyde, and 2-butenal. When 1 mm. of oxygen is present in the system, there is a considerable drop in the relative emission yield which reaches a value which is now independent of the amount of aldehyde added to acetone except for the possible slight contribution due to direct absorption of light quanta by the aldehyde itself. At a constant acetone pressure and incident intensity the emission yield observed in the presence of oxygen was found to be, within 5%, the same for all aldehyde-acetone mixtures. In addition, spectra taken of the emission of these mixtures on a Hilger F/4 provided with quartz optics indicated that the emission coincided with that for pure acetone in the presence of oxygen and, thus, may be reasonably ascribed to the fluorescence of acetone. Because the fluorescence and phosphorescence emitted from pure saturated aliphatic aldehydes have already been reported in some detail,^{5,9} these were not investigated any further. A search was, however, carried out for any light emitted from 2-butenal at 3130 Å. However, within the detection limit of our instrument, no phosphorescence or fluorescence was observed, indicating that the quantum yield of any light emitted from this compound must be less than 10^{-4} . Finally, it may be noted that none of the aldehydes quenches the phosphorescence emitted by biacetyl when irradiated at 3660 or 4358 Å.

In Fig. 2, $(Q_T)_0/Q_T$ has been plotted against the pressure of acetaldehyde, propionaldehyde, *n*-butyraldehyde, and 2-butenal. Q_T was simply obtained by subtracting the constant emission observed in acetone-aldehyde mixtures in the presence of oxygen from the total emission observed in the absence of oxygen. $(Q_T)_0$ is the emission calculated in the same way but for pure acetone.

2. **Acetone-Sensitized Decomposition of *n*-Butyraldehyde.**—Figure 3 gives the quantum yields of CO, CH₄, C₂H₄, C₂H₆, and C₃H₈ per quantum absorbed by

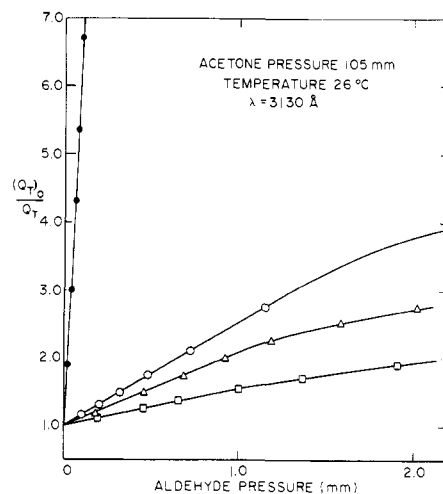


Fig. 2.—Plots of $(Q_T)_0/Q_T$ vs. the aldehyde pressure: ●, 2-butenal; O, *n*-butyraldehyde; Δ, propionaldehyde; □, acetaldehyde.

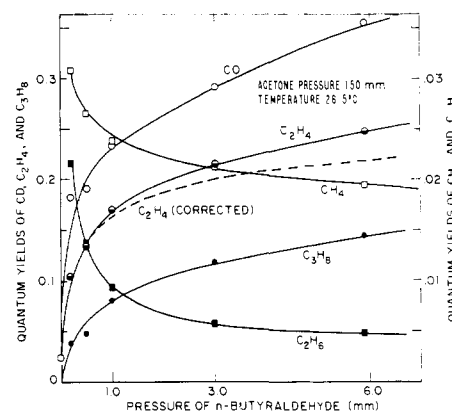


Fig. 3.—Yields of products per quantum absorbed by acetone vs. pressure of *n*-butyraldehyde.

acetone. At relatively high concentrations of *n*-butyraldehyde, there is some direct absorption by the latter compound. The contribution of this absorption to the ethylene formation was estimated by performing a few experiments on pure *n*-butyraldehyde at various pressures. The ethylene quantum yield, thus corrected, is given by the dotted line in Fig. 3. The ethylene yields given in parentheses in Table I have been similarly corrected for any contribution from the primary photolysis of the added aldehyde. It can be noted that, except at relatively high *n*-butyraldehyde pressures and high temperatures, the correction is quite small. The contribution of any direct photolysis to the yields of the other products cannot be accurately estimated because these are formed mainly in bimolecular reactions which involve radicals originating both from acetone and from butyraldehyde. The latter correction should, however, be of the same relative importance as that applied to the ethylene yield.

In Table I are represented the quantum yields of several products per quantum absorbed by acetone for a constant acetone-*n*-butyraldehyde mixture but at varying temperatures. The phosphorescence and fluorescence, emitted by pure acetone at the different temperatures, is also given in the same table. These values were obtained by measuring the light emitted by acetone at each temperature both in the presence and absence of oxygen. The phosphorescence is taken to be the difference between these two measurements.

(9) C. S. Parmenter and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **85**, 416 (1963).

TABLE I
 EFFECT OF TEMPERATURE ON THE ACETONE-PHOTOSENSITIZED DECOMPOSITION OF *n*-BUTYRALDEHYDE^a

| Temp., °K. | Φ_{CO} | Φ_{H_2} | $\Phi_{C_2H_4}$ | $\Phi_{C_2H_6}$ | $\Phi_{C_3H_4}$ | $\Phi_{C_3H_8}$ | $Q_T/(Q_T)_{30^\circ}$ | $Q_F/(Q_T)_{30^\circ}$ |
|--------------------|-------------|--------------|-----------------|-----------------|-----------------|-----------------|------------------------|------------------------|
| 299.5 | 0.356 | 0.0092 | 0.0194 | 0.0048 | 0.248 (0.220) | 0.145 | 1.0 | 0.11 |
| 299.5 ^b | n.d. | n.d. | n.d. | n.d. | 0.0323 (0.0036) | 0.0075 | 0.0 | 0.11 |
| 324 | 0.510 | 0.0083 | 0.0666 | 0.0124 | 0.200 (0.169) | 0.167 | 0.69 | 0.11 |
| 349 | 0.807 | 0.0102 | 0.205 | 0.0639 | 0.145 (0.112) | 0.190 | 0.35 | 0.115 |
| 372 | 1.11 | ... | 0.591 | 0.174 | 0.099 (0.064) | (0.183) | 0.18 | 0.12 |
| 398 | 1.58 | 0.0250 | 0.922 | 0.218 | 0.0628 (0.0246) | 0.269 | 0.082 | 0.13 |
| 422 | 2.00 | 0.0400 | 1.46 | 0.177 | 0.0524 (0.0116) | 0.476 | 0.043 | 0.13 |

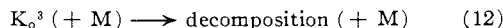
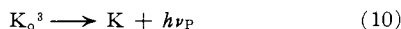
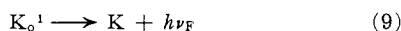
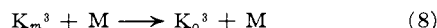
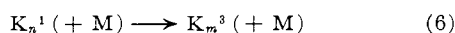
^a Pressure of acetone 150 mm.; pressure of *n*-butyraldehyde 6.0 mm.; the values of $\Phi_{C_3H_4}$, given in parentheses, are corrected for C_2H_4 formed from *n*-butyraldehyde in the direct photolysis. ^b Experiments performed in the presence of 2 mm. O_2 .

Results obtained in an experiment performed in the presence of oxygen are given in the second row of Table I. It can be noticed that the ethylene quantum yield corrected for any contribution of the direct photolysis of *n*-butyraldehyde is negligibly small when oxygen is present. In the latter experiment, the correction is a valid one because independent experiments, carried out on the photolysis of pure butyraldehyde, showed that addition of 5% oxygen reduces the quantum yield of ethylene by only 2%.

Discussion

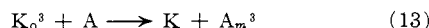
It is well established¹⁰ that, at 3130 Å., acetone emits light from two different excited states. There is a long-lived triplet state (lifetime 2×10^{-4} sec.)¹¹ which can be readily quenched by oxygen or by an increase in temperature, and a short-lived singlet state (lifetime $2-8 \times 10^{-6}$ sec.)^{10,12} which is not affected by oxygen and shows only a minor variation with temperature. It can be seen that the values of Q_F (fluorescence) and Q_T (phosphorescence), given in the last two columns of Table I, confirm these earlier findings.

The mechanism generally accepted¹³ to account for most observations is as follows



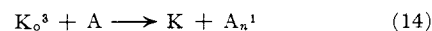
where K_n^1 is an acetone molecule excited to the n th vibrational level of the upper singlet state, K_m^3 is an acetone molecule excited to the m th vibrational level of the triplet state, and M is any molecule present in the system.

On the basis of the experimental observations reported in this study, the following step can be included when an aldehyde is added to the system



where A_m^3 is an aldehyde molecule excited to the m th level of the triplet state. The justification for this reaction is based on the fact that aldehydes quench only the phosphorescence emitted by acetone. If, in addition,

one invokes the Wigner spin-conservation rule for such a system, the product of this quenching process will be a triplet excited aldehyde molecule. The occurrence of a process such as



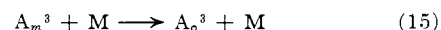
is, at any rate, excluded in view of the fact that no fluorescence is emitted by acetaldehyde, propionaldehyde, and *n*-butyraldehyde (see Results), the upper singlet states of which are known to fluoresce at 3130 Å. as well as at 3340 Å.⁵ with about the same quantum yield as acetone. A chemical reaction between a triplet acetone molecule and an aldehyde molecule in the ground state is also highly unlikely in view of the fact that the emission from triplet excited biacetyl, which has an even longer lifetime¹⁴ (2×10^{-3} sec.) than the triplet excited acetone molecule and may, thus, be expected to have at least as high a probability to react as acetone, is not quenched by any of the aldehydes.

On the basis of the simplified reaction mechanism given above, the following expression can be proposed:

$$(Q_T)_0/Q_T = 1 + [k_{13}]/(C[A])$$

where C represents the summation of the rates of the reactions which K^3 can undergo other than 13. It can be seen in Fig. 2 that plots of $(Q_T)_0/Q_T$ vs. the pressure of aldehyde at constant acetone pressure give good straight lines at low aldehyde pressures. However, a downward curvature becomes apparent at pressures of aldehydes above 1 mm. The probability of energy transfer (reaction 13) apparently varies according to the sequence 2-butenal > *n*-butyraldehyde > propionaldehyde > acetaldehyde. From the initial slopes, the following relative values for k_{13} can be deduced, taking a value of 100 for 2-butenal: 100:2.7:1.9:0.95. Thus, it can be seen that the presence of a double bond in the α,β -position strongly enhances the probability of triplet-state energy transfer from acetone to the aldehyde. An increase in chain length has a similar effect although to a much lesser extent. Taking a value for the mean lifetime of the triplet-state acetone molecule of 2×10^{-4} sec., about 100 collisions are required between acetone and 2-butenal to cause deactivation of excited acetone.

The curvature seen at high aldehyde pressures may be due, in part, to the possibility that some of the triplet aldehyde molecules, excited to the triplet state in reaction 13, may actually phosphoresce.



(10) For a review see: W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, *Chem. Rev.*, **56**, 49 (1956).

(11) W. E. Kaskan and A. B. F. Duncan, *J. Chem. Phys.*, **16**, 223 (1948).

(12) H. J. Groh, G. W. Luckey, and W. A. Noyes, Jr., *ibid.*, **21**, 115 (1953).

(13) See, for instance, J. Hecklen, *J. Am. Chem. Soc.*, **81**, 3863 (1959).

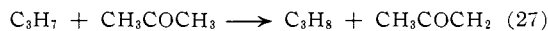
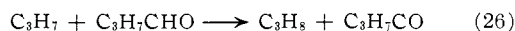
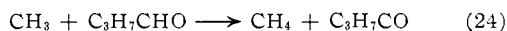
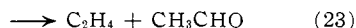
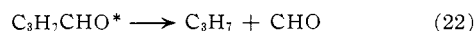
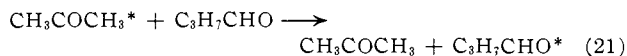
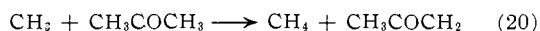
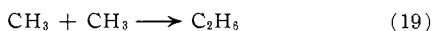
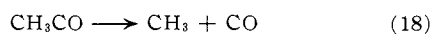
(14) H. J. Groh, Jr., *J. Chem. Phys.*, **21**, 674 (1953).

Because Q_T represents the total phosphorescence, any contribution from reaction 16 would tend to give values for k_{13} which are too low, especially at the higher aldehyde pressures where the relative contribution of reaction 16 to the total phosphorescence will be highest.

However, the fact that the total emission in acetone-butylaldehyde mixtures (Fig. 1) approaches the fluorescent yield curve demonstrates that the contribution of any phosphorescence emitted from *n*-butylaldehyde will be small. Also, recent studies⁵ on the photolysis of *n*-butylaldehyde and *n*-propionaldehyde did not reveal any noticeable phosphorescence even at 3340 Å. In the case of acetaldehyde, on the other hand, phosphorescent emission has been reported,^{9,15} although, even in this case, the phosphorescent yield accounts for less than 50% of the total emission yield.^{9,13} A decrease in phosphorescent yield with an increase in chain length of the excited molecule has also been reported for a series of ketones¹⁶ and can be ascribed to a shorter dissociative lifetime of the larger ketone or aldehyde.

Finally, it may be noted that the excited aldehyde molecules formed in reaction 13 will be excited to a low energy level because the lower vibrational levels of the triplet excited acetone from which this energy transfer may be expected to take place must correspond to wave lengths longer than those corresponding to the 0-0 level which has been tentatively placed¹⁰ at 3600 ± 200 Å.

Acetone-Sensitized Decomposition of *n*-Butylaldehyde.—In order to obtain additional information about the fate of A_m^3 formed in the energy-transfer reaction 13, the quantum yields of the gaseous products formed in the photolysis of acetone in the presence of relatively small concentrations of *n*-butylaldehyde have been determined. Neglecting any direct photolysis of *n*-butylaldehyde, the following simplified reaction mechanism previously proposed for the direct photolysis of acetone and *n*-butylaldehyde¹⁷ can account for most observations.



Although, in this reaction mechanism, $\text{CH}_3\text{COCH}_3^*$ stands for the acetone molecule excited to the upper singlet and/or triplet state, it follows, however, from the phosphorescent and fluorescent measurements described in the previous section that the electronically excited molecules participating in process 21 are in the

upper triplet state. It is clear that many other reactions, especially radical disproportionation and combination reactions, have been omitted from the reaction mechanism. All of these, however, will either make minor contributions to the products reported in this paper or will lead to the formation of products which have not been measured. At any rate, the proposed mechanism will suffice for the present discussion.

It can first be noted that, at 26.5°, the addition of less than 1 mm. of *n*-butylaldehyde to 150 mm. of acetone drastically reduces the quantum yields of methane and ethane which, on the basis of the proposed reaction mechanism, indicates that the decomposition of acetone is inhibited by the aldehyde. On the other hand, there is a simultaneous increase in the yield of ethylene and propane, rather strikingly demonstrating the occurrence of the decomposition processes 22 and 23 and, consequently, of the energy-transfer process 21. It is of interest to note the corrected ethylene plot of Fig. 3 levels off at about the same aldehyde pressure as the total emission curve for *n*-butylaldehyde (Fig. 1). It may be noted that the increase of CO can be mainly ascribed to process 22 followed in part by reactions 26 and 25.

That, as suggested before, the triplet state of acetone is involved in process 21 is shown by the data given in Table I. It can indeed be seen that the addition of a small amount of oxygen effectively quenches the formation of ethylene. Because the latter product is formed by a "molecular" elimination from *n*-butylaldehyde, this observation indicates either that the triplet *n*-butylaldehyde molecule is not formed because triplet acetone is removed by oxygen, or that the triplet *n*-butylaldehyde molecule is formed in the energy-transfer process but is quenched by oxygen. The first interpretation is apparently the correct one in view of the fact that (a) the efficiency of oxygen in quenching the phosphorescence emitted by acetone is at least an order of magnitude larger¹⁸ than the probability of process 21, and (b) the formation of ethylene in the photolysis of pure *n*-butylaldehyde at 3340 Å., which has been ascribed⁵ to a triplet excited molecule, is not readily quenched by oxygen (see Results). The involvement of the triplet-state acetone molecule in the energy-transfer process is further supported by the fact that, for a particular acetone-*n*-butylaldehyde mixture, the quantum yield of ethylene decreases gradually with an increase in temperature in much the same way as the phosphorescence emitted from pure acetone (column 8, Table I). In contrast, the fluorescence varies only slightly over the same temperature region and is, thus, not related to the formation of ethylene. As may be expected, the decrease of the quantum yield of ethylene with temperature is accompanied by an increase in the yield of CO, CH_4 , and C_2H_6 . The latter products are mainly formed as the result of the decomposition of an acetone molecule excited to an upper vibrational level of the triplet state^{1,8} which, at the higher temperatures, will display a lower phosphorescent yield and a lower probability of energy transfer because of the shorter dissociative lifetime. The fact that propane does increase over the entire temperature range can be ascribed to the fact that the diminishing importance of the dissociative process 22, at elevated temperatures, is offset by an increased probability of process 17 followed by

(15) E. Murad, *J. Phys. Chem.*, **64**, 952 (1960).

(16) P. Ausloos and E. Murad, *ibid.*, **65**, 1519 (1961).

(17) See, for instance, E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. 1, 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1954, pp. 312 and 318.

(18) See, for instance, W. A. Noyes, Jr., *Rad. Res. Suppl.*, **1**, 164 (1959).

reactions 24 to 27. This also accounts for the fact that the quantum yield of CO becomes larger than unity.

It would be of considerable interest to know the quantum yield of the energy transfer. However, no accurate estimate can be made at the present time, mainly because of the difficulty in establishing the quantum yield of process 22 and the number of aldehyde molecules which undergo an internal conversion to the ground state. It can, however, be noted that the quantum yield of ethylene reaches a value of 0.25 at the highest butyraldehyde pressures used in this study. Because the latter value is comparable to the quantum yield of

this process in the photolysis of pure butyraldehyde from 2537 (quantum yield = 0.3) to 3130 Å. (quantum yield = 0.165), it may be stated that, at sufficiently high concentrations of *n*-butyraldehyde, the quantum yield of process 21 may reach a value close to unity. This is not surprising in view of the fact that, at 3130 Å., the majority of the acetone molecules excited to the upper singlet state undergo an intersystem crossing to the triplet state.¹

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[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION, RICHMOND, CALIFORNIA]

Chain Transfer in the Autoxidation of Hydrocarbons Retarded by Phenol

BY J. R. THOMAS

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The proposal that the frequently observed concentration dependence of phenol in inhibited autoxidation of hydrocarbons arises from chain transfer between phenoxy radical and hydrocarbon has been tested. In carefully controlled experiments the reaction order with respect to tetralin is found to be 1.19 to 1.09, not 1.5 as is required by this mechanism. Study of the phenol-retarded oxidation rates of tetralin over about a 10⁴-fold range of phenol concentration demonstrates that the hydrocarbon chain-transfer mechanism cannot be of paramount importance. Data are presented reaffirming hydroperoxide chain transfer as the important cause of phenol kinetic order behavior. Rate constant estimates of $\geq 2 \times 10^6$ l. mole⁻¹ sec.⁻¹ for the phenoxy radical-hydroperoxide reaction and $\geq 10^9$ l. mole⁻¹ sec.⁻¹ for the reaction between phenoxy radical and alkylperoxy radical are confirmed.

Recently, two groups of investigators^{1,2} have proposed that chain transfer between inhibitor radical and hydrocarbon is the proper explanation of the inverse half-order dependence of the inhibited oxidation rate upon inhibitor concentration frequently observed and discussed.¹⁻⁴ In both instances, the evidence for this proposal is an observed 1.5 order of the phenol-inhibited rate with respect to hydrocarbon concentration using tetralin as well as other oxidizable substrates. This order of hydrocarbon concentration is that anticipated for special limiting conditions of the hydrocarbon chain-transfer mechanism as outlined approximately by Bickel and Kooyman.⁵ The work of the latter authors clearly shows that chain transfer between nonhindered phenoxy radicals and hydrocarbon can take place although the experimental conditions demonstrating the existence of this reaction were very different from those normally used to study chain termination by inhibitors.

This note presents additional data on the phenol-inhibited oxidation of tetralin. The data indicate that the reported^{1,2} hydrocarbon concentration order of 1.5 probably resulted from chain transfer between phenoxy radical and alkyl hydroperoxide, rather than with hydrocarbon. Further information about the surprisingly rapid rate of reaction between phenoxy radical and hydroperoxides, the importance of which has already been pointed out,⁶ is also presented.

Experimental

Materials.—Azobisisobutyronitrile (AIBN) was Eastman Kodak purified by recrystallization from methanol. Baker reagent grade phenol was recrystallized from hexane. DuPont tetralin was twice percolated through a 1.8-m. column packed with Davison activated silica gel. It was stored in the dark under oxygen-free nitrogen until used. Iodometric titration showed the residual hydroperoxide to be 10⁻⁴ M or less. Eastman Kodak chlorobenzene was treated once in an activated silica gel column.

Oxidation Procedure.—The oxidator consisted of a stirred 1-l. flask immersed in a carefully regulated water bath. 500 to 250 cc. of hydrocarbon solution containing the required amount of phenol was placed in the flask, and a moderate stream of oxygen was swept through the vapor space for 5 min. while the solution was stirred. After the system was thermally equilibrated (requiring about 20 min.), small aliquots of tetralin hydroperoxide and/or AIBN solution were added through a controlled opening. After the reaction was initiated with AIBN, the volume change was measured at 1- to 2-min. intervals by manually operating calibrated gas syringes to maintain constant pressure as indicated by a toluene manometer. Measurements were taken for about 30-min. periods. When curvature of the oxygen absorption *vs.* time plot occurred, the initial oxidation rate was determined from the initial slope utilizing, at most, points corresponding to hydroperoxide production of 4×10^{-4} M.

Results and Discussion

Proper design of experiments to study this problem and adequate interpretation of the results require an appreciation of the unusually rapid rate of reaction between phenoxy radical and hydroperoxide. An attempt to determine the order of magnitude of this rate constant⁶ indicated a value $\geq 2 \times 10^6$ l. mole⁻¹ sec.⁻¹. This can be compared with 12 l. mole⁻¹ sec.⁻¹ for cumylperoxy radical abstracting peroxidic hydrogen from tetralin hydroperoxide,⁷ 25.2 l. mole⁻¹ sec.⁻¹ for tetralyl

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