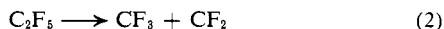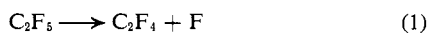rather than by loss of an F atom, although surprising at first sight, is consistent with the bond dissociation energies concerned. For the reactions

$$C_2F_5 \longrightarrow C_2F_4 + F \qquad (1)$$

$$C_2F_5 \longrightarrow CF_3 + CF_2 \qquad (2)$$

$D(C_2F_4-F) = \Delta H_f(C_2F_4) + \Delta H_f(F) - \Delta H_f(C_2F_5)$ and $D(CF_3-CF_2) = \Delta H_f(CF_3) + \Delta H_f(CF_2) - \Delta H_f(C_2F_5)$. Subtracting, $D(C_2F_4-F) - D(CF_3-CF_2) = \Delta H_f(C_2F_4) + \Delta H_f(F) - \Delta H_f(CF_3) - \Delta H_f(CF_2)$. Taking the best estimates,[8] $\Delta H_f(C_2F_4) = -152$, $\Delta H_f(F) = +18.9$, $\Delta H_f(CF_3) = -115 \pm 5$, and $\Delta H_f(CF_2) = -35$ kcal./mole, $D(C_2F_4-F)$ is greater than $D(CF_3-CF_2)$ by ~ 17 kcal./mole. A rather large error in $\Delta H_f(CF_3)$ or $\Delta H_f(CF_2)$ or a large difference in the activation energies

E_{-1} and E_{-2} for the reverse reactions would be needed to make reaction 1 competitive.

Appearance Potential Curves for $C_2F_5{}^+$. The appearance potential curves for $C_2F_5{}^+$ fragment ions were obtained from C_2F_6, C_2F_5H, C_3F_8, and C_4F_{10}. For these compounds the $C_2F_5{}^+$ ion curves showed considerable tailing and no reliable evaluation of the threshold for $C_2F_5{}^+$ formation could be made using the present technique.

A Pulse Radiolysis Study of Peroxy Radical–Aromatic Amine Reactions

A. MacLachlan

Contribution from the Radiation Physics Laboratory, Engineering Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware.
Received October 9, 1964

Pulse radiolysis is used to produce peroxy radicals under conditions that allow the mode and rate of their interaction with aromatic amines to be observed directly. Cyclohexyl peroxy radicals in cyclohexane form complexes with diphenylamine (DA) and N-methylaniline, while no complex is observed with N,N'-diphenyl-p-phenylenediamine (N,N'-DPPD) under the same conditions. Deuterium isotope effects are observed and used to interpret the results. α-Ethanol peroxy radicals in ethanol form long-lived complexes with all aromatic amines tested. Implications of these results to the basic mechanism of oxidation inhibition are discussed.

Introduction

Application of the technique of pulse radiolysis to the study of peroxy radicals[1] offers a unique opportunity to test some of the mechanisms proposed for inhibition of oxidation.[2,3] Previously, we had demonstrated that pulse radiolysis of cyclohexane containing dissolved oxygen produced high concentrations of cyclohexyl peroxy radicals and that their rate of disappearance could be followed spectroscopically. Cyclohexyl peroxy radicals produced in the concentration range of $> 10^{-4}$ M, decayed by second-order kinetics to produce cyclohexanone and cyclohexanol in equal quantities. The half-life under these conditions is a few milli-

(1) (a) R. L. McCarthy and A. MacLachlan, *Trans. Faraday Soc.*, **57**, 1107 (1961); (b) R. L. McCarthy and A. MacLachlan, *J. Chem. Phys.*, **35**, 1625 (1961).
(2) For a review, see K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).
(3) (a) G. S. Hammond, C. E. Boozer, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3238 (1955); (b) C. E. Boozer and G. S. Hammond, *ibid.*, **76**, 3861 (1954); (c) C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *ibid.*, **77**, 3233 (1955).

seconds ($k_0 = 2 \times 10^6$ l./mole) and corresponds to a disproportionation reaction retarded by a high steric factor. Cyclohexyl peroxy radicals absorb in the region of 2900 Å. Since most inhibitors (aromatic amines were used for this study) absorb strongly in this region, it is necessary to observe either the rate of elimination of inhibitor or the rate of formation of one of the reaction products. This paper presents direct spectroscopic evidence for the mechanism of amine–peroxy radical reactions and reports a method for obtaining absolute rate constants for the antioxidation process.

Experimental

Pulse Radiolysis Apparatus. The pulse radiolysis setup used for these experiments is shown schematically in Figure 1. A single 5-μsec. electron pulse is supplied by a Varian linear accelerator. Energy is nominally 8 Mev. with a beam current of 150 to 200 ma. Solutions in the radiolysis cell were changed after each electron pulse, using the reservoir flushing system shown also in Figure 1. Prior to filling the cell, oxygen was bubbled through the solutions for 5 min., and then the center movable dip tube was forced below the solution surface thus pumping the liquid into the cell. A constant pressure of oxygen was then used to drive fresh solution into the cell by operation of a solenoid valve on the exhaust side. Deoxygenated solutions were prepared by flushing with Airco 99.99% argon for 30 min. before cell filling.

Reagents. Cyclohexane was Eastman Spectrograde used without further purification. Ethanol was Pharmco U.S.P. absolute; 2-propanol and methanol
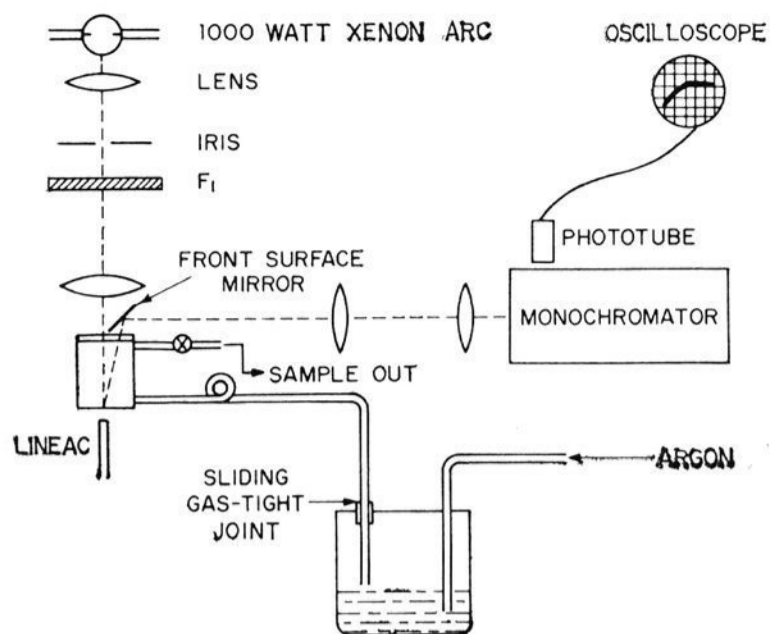
Figure 1. Pulse radiolysis apparatus.

Figure 2. Spectra of oxidation products.

were Fisher Certified reagent grade. N-Methylaniline and diphenylamine were Eastman chemicals.

Pure N,N'-diphenyl-p-phenylenediamine was prepared by Dr. C. W. Stephens by distillation of Eastman N,N'-diphenyl-p-phenylenediamine at reduced pressure under nitrogen followed by crystallization from methylene chloride. Material obtained in this manner is pure white and has remained so for 4 years.

N,N'-Diphenyl-p-quinodiimine (QI) was prepared by lead peroxide oxidation of N,N'-diphenyl-p-phenylenediamine in ethanol. It can also be prepared by radiolysis (using a G.E. resonant transformer supplying 2-Mev. electrons with a beam current up to 5 ma.) of an ethanol solution of N,N'-diphenyl-p-phenylenediamine saturated with oxygen. The bright orange crystals precipitate from solution on standing. The absorption spectrum of QI synthesized in this way is shown in Figure 2 in ethanol solution. The extinction coefficient at 4450 Å. is in good agreement with Pedersen's value.[4] Acidification with anhydrous HCl yields the stable Würster ion with the spectrum given in Figure 2.

Product Analysis. Cyclohexanol and cyclohexanone were analyzed using an F & M Model 400 gas chromatograph with hydrogen flame detection. A Perkin-Elmer 2-m. column R at 146° was used for the separation. Ten-μl. samples allowed direct analysis of 10^{-4} M solutions.

Results and Discussion

As pointed out in the Introduction, because of experimental difficulties attendant direct peroxy radical observation, it was found necessary to observe product formation. The following experimental work is aimed at proving the validity of this approach. The two aromatic amines studied in detail are diphenylamine (DA) and N,N'-diphenyl-p-phenylenediamine (N,N'-DPPD). Pulse radiolysis of either of these amines dissolved in cyclohexane containing oxygen results in color formation as shown in Figure 3. In both cases, at the concentration of amine used, the color-forming reaction is first order and is fast compared to the previously measured rate of disproportionation of cyclohexyl peroxy radicals.[1] Table I presents data showing that the rates of these reactions are dependent on the

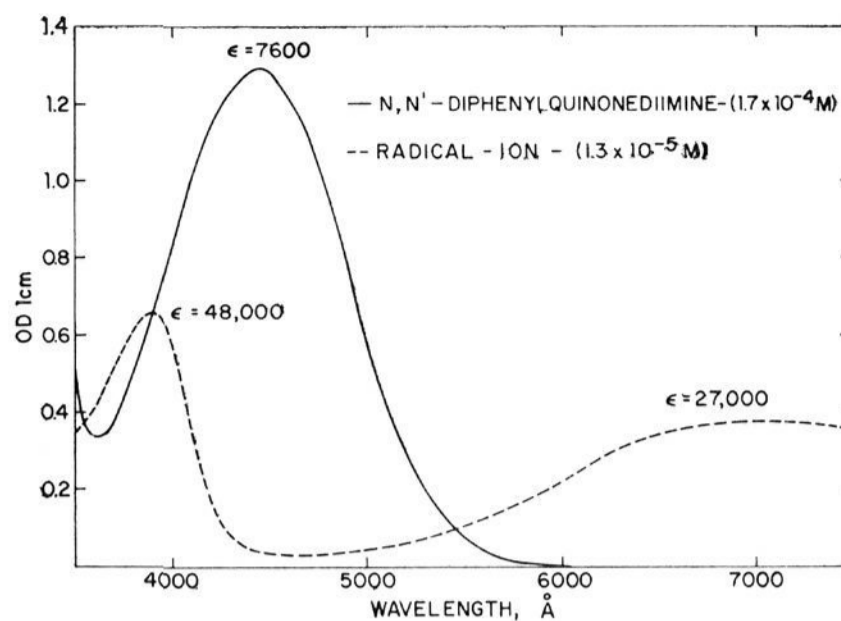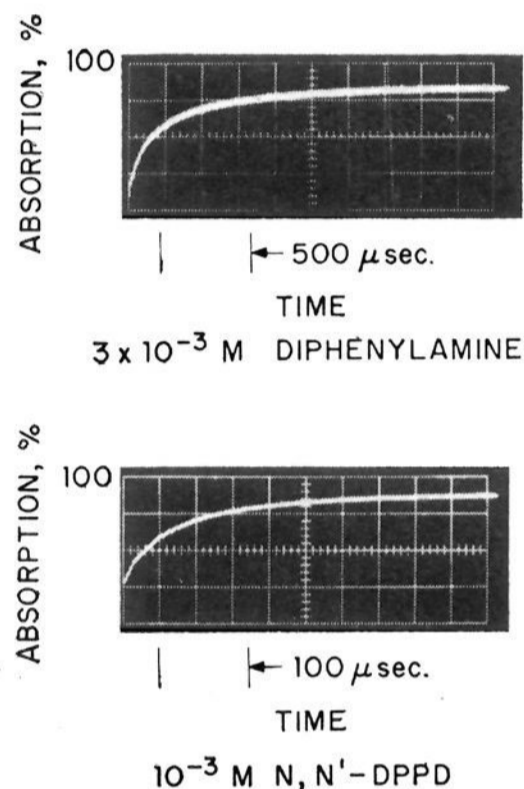(4) C. J. Pedersen, *J. Am. Chem. Soc.*, **79**, 2295 (1957).

Figure 3. Transient color formation curves.

starting amine concentration. Blank runs, where solutions were pulsed in the absence of oxygen, showed transient absorption at 3800 Å. with half-lives of the order of 20 μsec. These transients are most certainly the result of an inefficient reaction of the solvent radicals (including hydrogen atoms) with the aromatic amine solutes. This was easily shown by analysis with ultraviolet absorption spectroscopy where, at doses where 50% of N,N'-DPPD was allowed to react to produce QI in the presence of oxygen, under the same conditions in the absence of oxygen less than 1% reaction occurred. These results clearly show that oxygen must intercept some primarily formed radical and that only with peroxy radicals is there efficient reaction of the aromatic amines used in this work. Solubility limitations with N,N'-DPPD precluded a wide enough range of concentrations with this compound, but as shown in Table I, the proportionality is roughly first order. Since the peroxy radicals are produced at approximately 4 × 10^{-4} M and two peroxy radicals are expected to be required for each molecule of amine,[3] at 0.001 M the amine is significantly depleted and thus a direct proportionality is not expected.

Table I. Dependence of Color Formation on Amine Concentration in Cyclohexane Saturated with Oxygen

Amine	Concn., M	k_p,[a] sec.$^{-1}$ $\times 10^{-3}$
Diphenylamine	10^{-3}	4.3
	5×10^{-3}	13
	10^{-2}	27
N,N'-Diphenyl-p-	10^{-3}	35
phenylenediamine	1.4×10	58

[a] k_p is the pseudo-first-order rate constant. The absolute second-order rate constant k_{In} is obtained by dividing k_p by the concentration of amine.

At 5×10^{-3} and 10^{-2} M DA, the factor of two in rate is observed. These results can be explained in terms of Hammond's mechanism.[3]

$$RO_2\cdot + In \underset{k_D}{\overset{k_{In}}{\rightleftarrows}} C$$

$$C + RO_2\cdot \longrightarrow color$$
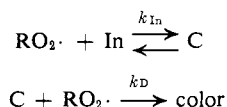
According to the preceding results, the formation of C must be rate determining. From these preliminary results, and keeping in mind an attempt to fit Hammond's mechanism, the following data would be desirable: (a) the nature of the colored product and the stoichiometry of its formation; (b) the fate of the peroxy radicals; and (c) proof for the existence or nonexistence of C.

Nature of the Colored Product. The colored product from DA, absorbing strongly at 3900 Å., does not lend itself to isolation and structure proof. It can be observed to fade significantly in a few seconds after it is formed, probably reflecting further oxidation and possibly photolysis by the analyzing light. However, the product from N,N'-DPPD was shown previously to be the corresponding N,N'-diphenyl-p-quinodiimine (QI)[3] and is in agreement with the results of this work. The absorption spectrum of authentic QI is shown in Figure 2 and is identical with the colored product formed by radiolysis of N,N'-DPPD in the solvents used. The G for the radiation-induced oxidation of N,N'-DPPD to QI in cyclohexane was found to be 2.5, corresponding to a stoichiometry of two peroxy radicals per oxidation since G (cyclohexyl peroxy radicals) = 5.1.[1a]

Table II. Products Formed with One-Electron Pulse.[a] Cyclohexane + O_2 + Inhibitor

Inhibitor	Concn., M	Products, M Cyclo-hexanone	Cyclo-hexanol
None		2.1×10^{-4}	2.2×10^{-4}
DA	10^{-2}	1.3×10^{-4}	1.6×10^{-4}

[a] The sample cell used for this radiation approximated the optical cell used in the pulse radiolysis experiments.

Fate of Peroxy Radicals. Product analyses are given in Tables II and III. Sensitive g.l.c. analysis allowed the products of one-electron pulse to be obtained.

The residual peroxy radicals not accounted for when inhibition is present probably form cyclohexyl hydroperoxide. The amines have a significant effect on the

Table III. Product Analyses. Cyclohexane + O_2 + Inhibitor[a]

Inhibitor	Concn., M	G (products) Cyclo-hexanone	Cyclo-hexanol
None		2.4	2.7
N,N'-DPPD	10^{-4}	2.1	2.0
DA	10^{-2}	1.7	1.5

[a] Resonant transformed irradiation, 2 Mev., 1 ma., with a dose rate of 0.64 w./cm.^{3}. Irradiation time was 15 sec.

products, but this analysis alone contributes little to understanding the transient process.

Complex Formation. Deuterium isotope effects present a straightforward test of the two possible ways by which the rate-determining reaction to form the complex C may occur. Since it has already been shown with both N,N'-DPPD and DA that the rate of final product formation observed by transient spectroscopy is directly proportional to the starting amine concentration, then an isotope effect would be observed for this rate if hydrogen abstraction from the NH grouping is the rate-determining step. Deuterium exchange is easily accomplished by shaking the amine cyclohexane solution with a massive excess of D_2O for 1 hr. prior to pulse radiolysis. Table IV lists the isotope results obtained.

Table IV. Isotope Effects in Cyclohexane

Inhibitor	Concn., M	$t_{1/2}$,[a] μsec.
N,N'-DPPD	10^{-3}	200
	10^{-3} (H_2O)[b]	180
	10^{-3} (D_2O)	550
DA	5×10^{-3}	530
	5×10^{-3} (H_2O)[b]	550
	5×10^{-3}	560

[a] Half-lives are given for ease of comparison. [b] Solutions saturated with H_2O were run as controls to demonstrate that water does not affect the rate or deplete the amine concentration.

Clearly, with these two amines, the two basic types of behavior are observed. N,N'-DPPD exhibits a substantial isotope effect, while DA has none. Consideration of the lack of an isotope effect and the first-order dependence on DA concentration makes a complex likely for this inhibitor. No complex in cyclohexane is needed to explain the action of N,N'-DPPD.

Ethanol Peroxy Radicals. Cyclohexane is unsatisfactory for examining many amine inhibitors because of poor solubility characteristics. It seemed desirable to work with a more polar solvent, and ethanol was chosen for investigation. Ethanol produces almost exclusively the α-ethanol radical[5] under irradiation and in the presence of dissolved oxygen exhibits the expected peroxy radical at 2900 Å. with the excellent second-order kinetics shown in Figure 4. The measured rate constant of $1.2 \pm 0.4 \times 10^8$ M^{-1} sec.$^{-1}$ is substantially faster than that for cyclohexyl peroxy radicals but is still some 100 times below a diffusion-controlled rate. This rate constant is calculated from the transient data of Figure 4 and the G yield for the

(5) (a) L. M. Dorfman and I. A. Taub, *J. Am. Chem. Soc.*, 85, 2370 (1963); (b) I. A. Taub and L. M. Dorfman, *ibid.*, 84, 4053 (1962).

α-ethanol radical production given by Dorfman.[5] Pulse radiolysis of ethanol–oxygen mixture containing N,N'-DPPD gave the results shown in Table V. Blank experiments in the absence of oxygen gave the same results as were obtained in the case of cyclohexane, and again, no significant amount of amine reacts showing that the peroxy radical derived from the solvent is the important reactive species and not one of its precursors.

Table V. Pulse Radiolysis of N,N'-DPPD Observing QI Formation at 4400 Å.

N,N'-DPPD concn., M	Formation solvent	$t_{1/2}$, μsec.
10^{-3}	Cyclohexane	200
5×10^{-4}	Ethanol	60,000
10^{-2}	Ethanol	42,000
10^{-2}	2-Propanol	100,000
10^{-3}	Ethanol (0.6 M sodium ethoxide)	1,500,000

Ethanol peroxy radicals disproportionate with a half-life of 20 μsec. at the concentration formed, and yet the QI formation kinetics are first order, as shown in Table V, and essentially independent of N,N'-DPPD concentration. It is apparent that a relatively stable complex has formed which does not absorb at 4400 Å., and its first-order decomposition to QI is the rate-determining step. No assessment of k_{In} is possible in neutral ethanol.

This conclusive evidence for complex formation represents an added step in the mechanism of anti-oxidation which must be considered. That is

$$RO_2\cdot + C \longrightarrow C' \longrightarrow QI$$
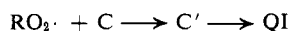
The effect of the additional solvent 2-propanol and the effect of water and sodium ethoxide on the rate of decomposition of the complex will be discussed in the next section. Qualitatively, DA behaved in the same manner. The half-life for color formation was approximately 20 msec. with a maximum at 4500 Å. rather than at 3900 Å. Observation at 3900 Å. showed a fast rise with a lifetime of 20 μsec. and no further increase at this wave length. Owing to the low intensity of this absorption and the unknown nature of the final colored product, no further studies were performed with diphenylamine in ethanol.

Other Solvents. N,N'-DPPD was also examined in 2-propanol. Results shown in Table V are qualitatively similar to ethanol. It was suspected that water might influence the rate of breakdown of the complex, and this was verified. In 20% ethanol–water, the rate of color formation increased by a factor of 25 over pure ethanol. In both methanol and 2-propanol, a very fast decay between 5000 and 7000 Å. could be observed, which is probably the Würster ion. The fast decay of this ion does not correspond to the rate of QI formation but rather leads to an intermediate which decays slowly to QI. Addition of 2% water to 2-propanol removed the Würster ion and yielded a product kinetic curve that seems to resolve into two first-order processes indicating the presence of two intermediates. Verification that these intermediates were influenced by some acid–base equilibrium was accomplished by addition of
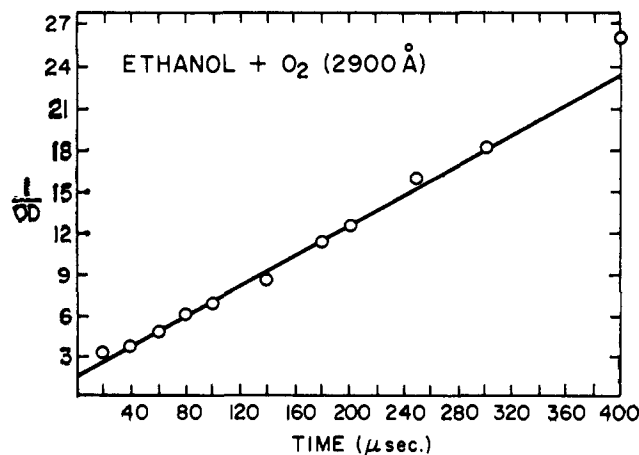

Figure 4. Second-order plot of ethanol peroxy radical decay.

0.6 M sodium ethoxide to an ethanol solution of N,N'-DPPD noting that the QI formation lifetime was now increased to more than 1.5 sec. as opposed to 40–60 msec. (Table V).

N-Methylaniline in Cyclohexane. N-Methylaniline was examined with cyclohexyl peroxy radicals and yielded evidence for complex formation. Table VI

Table VI. Rate of Color Formation with Cyclohexyl Peroxy Radicals and N-Methylaniline

N-Methylaniline concn., M	k,[a] sec.$^{-1}$
10^{-3}	0.9×10^{3}
5×10^{-3}	1.1×10^{3}
1.6×10^{-2}	1.2×10^{3}

[a] k is the first-order rate constant for color kinetics at 3600 Å.

presents the lifetime for color formation at 3600 Å. as a function of concentration. Even in cyclohexane, the breakdown of C' can be rate determining.

Conclusions

Providing the rate of color formation can be shown to be first order in inhibitor concentration, the pulse radiolysis method yields the absolute rate constant for antioxidation directly. However, solubilities and solvent structure play an important part in determining the feasibility of these measurements, and in many cases, the breakdown of a molecular complex is rate determining.

The observation of a complex agrees with the general mechanism proposed by Hammond,[3] but the isotope effect for N,N'-DPPD in cyclohexane does not. Isotope effects have been used to prove or disprove the rate-determining steps for antioxidation with a limited number of antioxidants in a number of different substrates.[3,6-11] Complex formation or lack of it has also been studied.[12,13]

(6) J. R. Shelton and D. N. Vincent, *J. Am. Chem. Soc.*, **85**, 2433 (1963).
(7) C. J. Pedersen, *Ind. Eng. Chem.*, **48**, 1881 (1956).
(8) J. R. Shelton and E. T. McDonel, *J. Polymer Sci.*, **32**, 75 (1958).
(9) J. R. Shelton, E. T. McDonel, and J. C. Crano, *ibid.*, **42**, 289 (1960).
(10) K. U. Ingold and I. E. Puddington, *Ind. Eng. Chem.*, **51**, 1322 (1959).
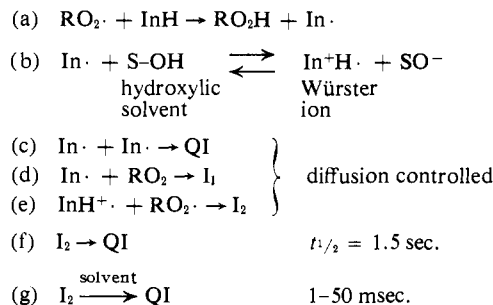(11) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **40**, 1851 (1962).

This work, using only three aromatic amines of similar structure, has encountered virtually all possible combinations of behavior for inhibition. There is no doubt that complexes form, and on the basis of the limited data in this study, it would appear that polar solvents enhance their stability. However, even in cyclohexane, N-methylaniline was shown to yield a short-lived complex which precluded determination of the absolute rate constant for the peroxy radical reaction.

Diphenylamine reacted in a rate-controlling step with peroxy radicals but did not exhibit an isotope effect. This is in agreement with Hammond's early work; and while it does not prove the equilibrium nature of the peroxy radical–amine reaction, it does prove that a complex is formed.

In all cases examined, complexes were formed in ethanol. The lifetimes of these complexes are strongly influenced by the solvent. A tentative mechanism which explains the result in alcohols is shown in Scheme I. In the presence of strong base, I_2 formation is favored. In neutral solution, both I_1 and I_2 are formed, and in acidic media the Würster ion is formed directly. Reaction a is written as a hydrogen abstraction because the yield of Würster ion is not enough to explain the total amount of QI formed and because this ion can be suppressed completely by added water. The difference between I_1 and I_2 may be in the position of

(12) J. R. Thomas, *J. Am. Chem. Soc.*, 85, 591, 593, 2166 (1963).
(13) J. R. Thomas and C. A. Tulman, *ibid.*, 84, 2930 (1962).

Scheme I

(a) $RO_2 \cdot + InH \rightarrow RO_2H + In \cdot$

(b) $In \cdot + S\text{-}OH \rightleftarrows In^+H \cdot + SO^-$
hydroxylic   Würster
solvent   ion

(c) $In \cdot + In \cdot \rightarrow QI$ ⎫
(d) $In \cdot + RO_2 \rightarrow I_1$ ⎬ diffusion controlled
(e) $InH^+ \cdot + RO_2 \cdot \rightarrow I_2$ ⎭

(f) $I_2 \rightarrow QI$ $t_{1/2} = 1.5$ sec.

(g) $I_2 \xrightarrow{\text{solvent}} QI$ 1–50 msec.

attachment of RO_2. Reaction c is needed to explain the 20 to 30% QI formation that occurs as a rapid reaction following the beam pulse.

From the effect of acid and base on the product formation rates in alcohols, it should be possible to obtain the absolute rate of ethanol peroxy reaction with N,N'-DPPD by working an acidic media where the Würster salt is stable, and only one peroxy radical is required per inhibition. Preliminary experiments indicate this approach will work, and a rate constant of approximately 10^7 l./mole sec. was obtained for rate of Würster ion formation in ethanol containing dissolved oxygen.

The Exchange Reaction of Ethyl Iodide and Iodine[1,2]

Edward D. Cohen[2] and C. N. Trumbore

Contribution from the Department of Chemistry, The University of Delaware, Newark, Delaware. Received August 19, 1964

The thermal-exchange reaction of ethyl iodide and iodine was investigated in the liquid phase. The exchange rate was independent of iodine concentration from 10^{-8} to 10^{-3} M and had an average value of 0.50×10^{-6} M/hr. in CCl_4 solvent at 23°. The over-all exchange rate was dependent on ethyl iodide concentration and may be expressed by $R_{ex} = k(EtI)^2$. This rate law was applicable from 0 to 40° with an activation energy of 22 kcal./mole. Isopropyl iodide was found to exchange at a significantly lower rate. The rate-controlling step is postulated to be the slow formation of diethyl iodonium iodide followed by a fast attack of iodine on the iodonium iodide whose decomposition leads to exchange. The implications of this study on the radiolysis reaction of ethyl iodide are discussed.

The thermal-exchange reaction between ethyl iodide and iodine has been studied by several authors[3–8]

since the initial study by Lind, *et al.*,[9] in 1936. The main feature of these studies has been the irreproducibility of the data which was obtained and has resulted in very few kinetic treatments of this system.

At iodine concentrations of 10^{-3} to 10^{-4} M and 6 M in ethyl iodide and from 40 to 70°, Darbee and Harris[7] were unable to obtain consistent exchange results. At concentrations greater than 10^{-2} M I_2, an exchange rate law of $R_{ex} = k(I_2)$ was obtained, but no mechanistic interpretation was presented. It was stated that the exchange probably involved the addition complex of ethyl iodide and iodine. At concentrations of 10^{-4} to 10^{-5} M, Herbst[8] obtained two different rate laws for the same system depending on his method of solution preparation. If the iodine was produced by decom-

(3) R. E. Bujake, W. T. Pratt, and R. M. Noyes, *J. Am. Chem. Soc.*, 83, 1547 (1961).
(4) R. M. Noyes, *ibid.*, 70, 2614 (1948).
(5) R. M. Noyes, *ibid.*, 75, 767 (1953).
(6) M. B. Neiman, V. B. Miller, and Y. M. Shapovalov, *Zh. Fiz. Khim.*, 30, 492 (1956).
(7) L. R. Darbee and G. M. Harris, *J. Phys. Chem.*, 61, 111 (1957).
(8) R. Herbst, *Anales Fac. Quim. Farm. Univ. Chile*, 12, 207 (1960).
(9) D. E. Hull, C. H. Shuflett, and S. C. Lind, *J. Am. Chem. Soc.*, 58, 535 (1936).