minute. To start a run, 10 ml. of the solvent was introduced into the reaction vessel and allowed to equilibrate. The shaking was momentarily interrupted while a sample of α-phenethyl chloroglyoxalate (1.9–3.1 mmoles) was introduced by means of a hypodermic syringe through a serum bottle stopper on the side-arm of the flask. Shaking was resumed and the volume of the evolved gases was read at various intervals. The bath temperature was maintained within ±0.1°. The buret jacket temperature was 20.00 ± 0.05°.

First-order rate constants were evaluated from plots of log $(V_\infty - V)$ against time.[30] Straight lines were obtained up to 80% reaction in some of the faster runs. In all the runs, 0.5–1.5 g. of powdered Pyrex glass was added to the reaction vessel in order to prevent supersaturation of the solvent by the evolved carbon monoxide and carbon dioxide. The powdered glass had no effect on the rate constants. After each run the reaction flask and the powdered glass were cleaned thoroughly by rinsing with acetone followed by water. The flask was then soaked in chromic acid solution and finally in distilled water. The water was removed by flaming. The rate constants so obtained are presented in Table IV. Data for typical runs are reproduced in Table VI.

From a plot of log k *vs.* $1/T$ the rate data for the decompositions in nitrobenzene were fitted to the Arrhenius equation. From the experimental E_{act} obtained (19.8 kcal./mole) an activation enthalpy of 19.0 kcal./mole and entropy of activation of −27 e.u. were calculated for $T = 381.4$°K. from the relationships $\Delta H^{\ddagger} = E_{act} - RT$ and $\Delta S^{\ddagger} = R \ln k - R \ln (k'T/h) + \Delta H^{\ddagger}/T$. Uncertainties in E_{act} and $\Delta H^{\ddagger}$ are estimated at ±1 kcal./mole and, in $\Delta S^{\ddagger}$, at ±2 e.u.

(30) V_∞ was calculated from the weight of the chloroglyoxalate introduced into the reaction vessel. In some of the faster runs, V_∞ was determined experimentally and agreed quite well with the calculated value.

TABLE VI

SAMPLE RATE DATA FOR THE DECOMPOSITION OF α-PHENETHYL CHLOROGLYOXALATE IN NITROBENZENE AT 108.3°

$k = 1.39 \times 10^{-4}$ sec.$^{-1}$, init. concn. of chloroglyoxalate, 2.06 mmoles			$k = 1.36 \times 10^{-4}$ sec.$^{-1}$, init. concn. of chloroglyoxalate, 3.11 mmoles		
t, min.	$(V_\infty - V)$	log $(V_\infty - V)$	t, min.	$(V_\infty - V)$	log $(V_\infty - V)$
0	127.8	2.107	0	195.2	2.290
12	119.6	2.077	6	188.5	2.275
24	109.1	2.038	12	180.6	2.257
36	99.3	1.997	18	172.1	2.236
48	89.6	1.952	24	163.8	2.214
60	80.6	1.906	30	155.6	2.192
72	72.6	1.861	36	148.8	2.172
84	65.4	1.816	42	140.2	2.147
96	59.1	1.771	48	132.8	2.123
108	53.6	1.729	54	126.1	2.101
120	48.7	1.688	60	119.7	2.079
132	44.1	1.644	66	113.5	2.055
144	40.2	1.604	72	107.6	2.028
156	36.7	1.564	78	102.4	2.011

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

Stability of Cumylperoxy Radical–Pyridine Charge-Transfer Complex

BY J. R. THOMAS

RECEIVED JULY 3, 1962

In oxidizing cumene the steady-state cumylperoxy radical concentration can be determined by electron spin resonance. In the presence of pyridine, a strong donor molecule for charge-transfer complex formation, the total free-spin concentration should be increased by the term $[RO_2\cdot]_{s.s.}[\text{pyridine}]K$, where K is the equilibrium constant for complex formation $RO_2\cdot$ + pyridine $\rightleftarrows$ $[RO_2^-\cdots{}^+\text{pyridine}]$. At 57 and 40° no increased free-spin concentration is observed in 1 *M* pyridine solutions. It is concluded that K must be less than 0.4 l./mole. Measurement of the time required to reach steady-state cumene oxidation at 57° in the presence of pyridine leads to a similar conclusion.

Porter and Smith[1] have explained the influence of chaperon molecules upon the recombination rate of iodine atoms in terms of a charge-transfer complex intermediate between the two species. With such materials as ethyl bromide and benzene, Grover and Porter[2] and Strong, *et al.*,[3,4] have observed transient optical absorption bands which have been shown to be due to this type of iodine atom complex. Russell[5] has shown that pronounced solvent effects upon chlorination reactions can be explained in terms of chlorine-atom substrate complexes of similar nature. As a result of kinetic studies of hydrocarbon oxidation inhibition by aromatic amines and phenols, Boozer and Hammond[6,7] have postulated the rapid, reversible formation of charge-transfer complexes between such inhibitors and alkylperoxy radicals as the critical step in the inhibition mechanism. Recent studies in this field[8] have confirmed the kinetic results of these investigators which, to date, can only be reasonably explained in terms of such complex species.

This paper reports studies of cumene oxidation by electron spin resonance and kinetic techniques leading to the conclusion that the equilibrium constant for complex formation between cumylperoxy radical and pyridine is small.

(1) G. Porter and J. A. Smith, *Proc. Roy. Soc.* (London), **A261**, 28 (1961).
(2) T. A. Grover and G. Porter, *ibid.*, **A262**, 476 (1961).
(3) S. J. Rand and R. L. Strong, *J. Am. Chem. Soc.*, **82**, 5 (1960).
(4) R. L. Strong, S. J. Rand and J. A. Britt, *ibid.*, **82**, 5053 (1960).
(5) G. A. Russell, *ibid.*, **80**, 4987 (1958).
(6) C. E. Boozer and G. S. Hammond, *ibid.*, **76**, 3861 (1954).
(7) C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3233 (1955).
(8) J. R. Thomas and C. A. Tolman, *ibid.*, **84**, 2930 (1962).

Experimental

Materials.—Cumene was Eastman white label passed through a silica column. Benzene and pyridine were J. T. Baker research grade. Azobisisobutyronitrile was recrystallized from methanol.

Electron Spin Resonance Studies.—A Varian Model 4500 spectrometer with 100 kc. modulation was used. The oxidation reactor was a 5-liter flask equipped with a bubbler for saturating the solution with oxygen. The reactor was located immediately above the microwave cavity. Solution was flowed through the cavity *via* a quartz tube. At flow rates of the order of 1 l./min. the intensity of the resonance was independent of rate. At 0.2 l./min. the intensity was reduced. When flow through the cavity was stopped, the resonance disappeared completely in several minutes.

The experimental arrangement was calibrated with diphenyl nitric oxide solutions of known concentration. Radical concentrations were determined by double integration of the derivative line. Reproducibility was ±20% for identical experiments. The absolute radical concentrations are estimated to be within ±50%.

Oxidation Studies.—The oxidator was a stirred reactor in conjunction with a sensitive gasometer. The reactor, which served also as the gas reservoir, was completely immersed in a regulated water bath. In all cases the system was brought to thermal equilibrium without initiator. At time zero a small volume of prewarmed initiator solution was injected into the system throughout a controlled opening. Carefully done, this caused very slight upset to the system.

Results and Discussion

At low temperatures the oxidation of cumene by molecular oxygen is a simple chain reaction. When

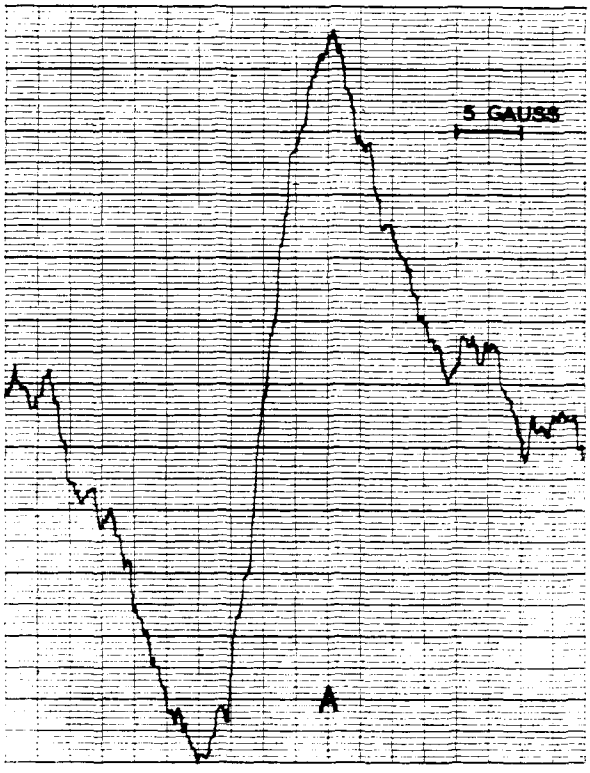

Fig. 1.—E.s.r. spectrum of cumylperoxy radical.

oxidation is initiated with a suitable material such as azobis-isobutyronitrile (AIBN), the mechanism is

$$\text{AIBN} \xrightarrow{O_2} RO_2\cdot \qquad k_1 \quad (1)$$

$$RO_2\cdot + RH \longrightarrow R\cdot + RO_2H \qquad k_p \quad (2)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad k_3 \quad (3)$$

$$RO_2\cdot + RO_2\cdot \longrightarrow X \qquad k_t \quad (4)$$

This leads to expression 5 for the steady-state con-

$$[RO_2\cdot]_{s.s.} = [k_1[\text{ABN}]/2k_t]^{1/2} \qquad (5)$$

centration of cumylperoxy radicals. In the presence of a complexing material such as pyridine, establishment of equilibrium 6 would increase the total concentration

$$RO_2\cdot + \text{Py} \rightleftarrows [RO_2\cdot^- \ldots \text{Py}^+]K \qquad (6)$$

of paramagnetic species to that given by (7). Conse-

$$\text{Total free-spin concn.} = [RO_2\cdot]_{s.s.}(1 + K[\text{Py}]) \qquad (7)$$

quently, by observing the change in concentration of paramagnetic material in the presence of pyridine, the value of K can be determined.

Lebedev, Tsepalov, and Shlyapintokh[9] have shown that the steady-state cumylperoxy radical concentration can be determined by electron spin resonance in oxidizing cumene at moderate temperatures. At the time the report of their work became available, similar results had been obtained in our laboratories. Figure 1 shows the resonance absorption of cumylperoxy radical obtained in oxidizing 2 M cumene in benzene at 74° with 0.05 M AIBN initiator. The resonance absorption corresponds to an $RO_2\cdot$ concentration of 4.1×10^{-6} M. Using $2k_t = 7.4 \times 10^4$ from the rotating sector work of Melville and Richards[10] and $k_1 = 7.2 \times 10^{-5}$ sec.$^{-1}$ obtained by use of diphenyl nitric oxide as a scavenger,[8] equation 5 predicts a concentration of 6.9×10^{-6} M. The value of $2k_t$ used is twice that given by the authors to correct for inefficiency in initiation by AIBN due to the solvent cage effect. Bartlett has suggested[11] that

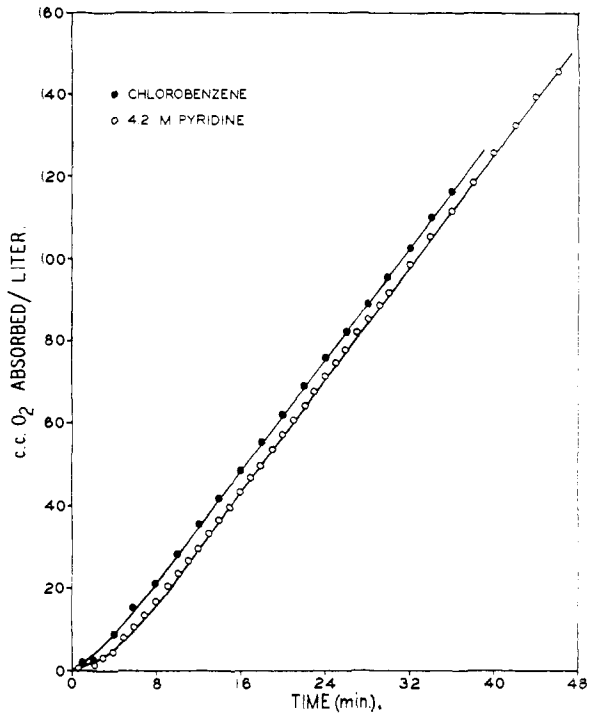

Fig. 2.—O_2 absorption *versus* time, 4 M cumene, 4×10^{-3} M AIBN, 1 atm. O_2, 57.0°.

this value should be increased by an additional factor of about 2.2 to account for interactions which do not result in chain termination,[12,13] which would bring experiment and theory into substantial agreement. Similar agreement has been observed at lower temperatures and different AIBN concentrations.

Electron spin resonance studies in oxidizing cumene containing up to 1 M pyridine at temperatures of 57 and 40° showed no increase in total detectable paramagnetic species over that of pyridine free solutions to within experimental error. The average deviation of estimating radical concentrations was ±20%. Consequently, by these measurements, K could not have a value in excess of 0.4 l. mole^{-1}. Success with this method of estimating the concentration of charge-transfer species obviously demands that the line width of the complex absorption be narrow enough to permit detection. While we are unaware of any reason to expect an undetectably wide line from such a species a second method of estimating the extent of complex formation was used.

This method involves determination of the time required for oxidation to reach its steady-state rate after addition of initiator. From the previous discussion it follows that in the presence of pyridine the $RO_2\cdot$ concentration as a function of time is given by (8). At 57° no effect in excess of experimental reproducibility

$$[RO_2\cdot]_t = [RO_2\cdot]_{s.s.} \tanh\left[\frac{(2k_1[\text{AIBN}]k_t)^{1/2}t}{1 + K[\text{Py}]}\right] \qquad (8)$$

was noted at pyridine concentrations as high as 4.2 M. Oxygen absorption *versus* time is plotted in Fig. 2 for typical experiments with and without pyridine. The results lead to the conclusion that K is less than about 1 l. mole^{-1} in agreement with the e.s.r. measurements. Appropriate values of k_t and $2k_t$ are 7.7×10^{-6} sec.$^{-1}$ and 7.2×10^4 mole l.$^{-1}$ sec.$^{-1}$, respectively.

Pyridine is known to form strong charge-transfer complexes with acceptors such as iodine. Extrapolating

(9) V. S. Lebedev, V. F. Tsepalov and V. Y. Shlyapintokh, *Proc. Acad. Sci. U.S.S.R., Phys. Chem.*, **139**, No. 1-6, 646 (1961). Consultants Bureau English Translation.

(10) H. W. Melville and S. Richards, *J. Chem. Soc.*, 944 (1954).

(11) P. D. Bartlett, private communication.

(12) H. S. Blanchard, *J. Am. Chem. Soc.*, **81**, 4548 (1959).

(13) T. G. Traylor and P. D. Bartlett, *Tetrahedron Letters*, **24**, 30 (1960).

the data of Reid and Mulliken[14] to 57° yields an equilibrium constant for complex formation of 80 l. mole^{-1}. Since the $RO_2\cdot$ radical is believed to have an electron affinity of 70 kcal. mole^{-1},[15] while this value for iodine is 54.6 kcal. mole^{-1},[16] it is surprising that the cumylperoxy radical–pyridine complex appears weak. Other factors, however, influence complex stability.

The choice of pyridine as a representative donor may be criticized for the present purpose of evaluating the extent of complex formation between cumylperoxy radicals and oxidation inhibitors. Unfortunately, the aromatic amine oxidation inhibitors themselves cannot be used in these types of studies because they both lower the steady state $RO_2\cdot$ concentration and give rise to relatively high concentrations of disubstituted nitric oxide radicals.[8] E.s.r. studies with triphenylamine, similar to those described above for pyridine, have been conducted with the result that K can be said to be less than 4 l. mole^{-1} at 57°. Studies with N,N-dimethylaniline and diphenylmethylamine have not yielded interpretable results because of complications which they produce upon the oxidation rate when used at high concentrations.

With iodine the ΔH values for complexes with pyridine (−7.8 kcal. mole^{-1}), N,N-dimethylaniline (−8.2 kcal. mole^{-1}) and trimethylamine (−12.0 kcal. mole^{-1}) parallel basicity, pK values of 5.19, 5.21, and 10.7, respectively,[17] while formation constants at 57° are 80, 6.3, and 1700 l. mole^{-1}, respectively. Less basic diphenylamine, pK = 0.85, would be expected to be a poorer n-donor than pyridine; and it seems doubtful that its formation constant for complexing with cumylperoxy radical would be significantly larger than that of pyridine.

With regard to the charge-transfer complex mechanism of oxidation inhibition, these results indicate that the termination reaction 9 must be very rapid. For diphenylamine the product Kk_9 has been shown[8] to

$$RO_2\cdot + [RO_2\cdot \ldots I_n] \rightarrow \times \quad k_9 \qquad (9)$$

have a value of 3.6×10^9 l.^{2} mole^{-2} sec.$^{-1}$. With K small, k_9 must be close to the diffusion limited value. The possibility remains, of course, that the charge-transfer complex mechanism is incorrect and the kinetic observations which support it should be explained by an alternate mechanism. To date, however, no plausible alternate has been suggested.

NOTE ADDED IN PROOF.—For discussion of the nil complex formation between oxygen and pyridine see H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, **82**, 5969 (1960).

Acknowledgment.—The author is indebted to Dr. J. C. Baird for assistance with the e.s.r. measurements and to Professor P. D. Bartlett for helpful discussion concerning the status of the termination reaction of cumylperoxy radicals.

(14) C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3869 (1954).
(15) H. O. Pritchard, *Chem. Revs.*, **52**, 529 (1953).
(16) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950).
(17) H. Tsubomura, *ibid.*, **82**, 40 (1960).

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

Oxidation Inhibition by Trialkylamines

BY J. R. THOMAS

RECEIVED JULY 3, 1962

Trialkylamines at low concentrations inhibit the oxidation of cumene in accordance with the Boozer–Hammond mechanism. At higher concentrations, however, the inhibited rates become independent of amine concentration. This behavior is taken as evidence that cumylperoxy radical–trialkylamine complexes undergo chain propagation and self-termination reactions in addition to the simple Boozer–Hammond reactions of strong inhibitors such as diphenylamine. Electron spin resonance studies indicate that the equilibrium constants for complex formation of cumylperoxy radical with triethylamine and tri-n-butylamine are less than 53 and 86 l. mole^{-1}, respectively.

Trialkylamines are recognized inhibitors of high temperature gas-phase hydrocarbon oxidation.[1,2] However, to our knowledge, their study as liquid-phase inhibitors has not been reported. Their behavior is of particular interest in view of their great tendency to act as donors in charge-transfer complex formation. The Boozer–Hammond[3] mechanism of oxidation inhibition postulates such complex formation in a critical step as formulated. This paper describes studies of triethyl- and tri-n-butylamines as inhibitors for the oxidation of

$$RO_2^0 + I_n \rightleftarrows [RO_2^- \ldots I_n^+]$$
$$[RO_2^- \ldots I_n^+] + RO_2\cdot \longrightarrow x$$

cumene and interprets the results in terms of charge-transfer complexes of these materials with cumylperoxy radical.

Experimental

The apparatus and techniques for oxidation rate and electron spin resonance (e.s.r.) measurements have been described.[4,5] Cumene was Eastman white label material passed through a silica column. Azobisisobutyronitrile was recrystallized from methanol. Triethyl- and tri-n-butylamines were Eastman white label chemicals purified by distillation.

Results and Discussion

Trialkylamines are reasonably active inhibitors for the oxidation of cumene at 70°. Initial inhibited oxidation rates, initiated by azobisisobutyronitrile (AIBN), are proportional to [AIBN]$^{1/2}$ as required by the Boozer–Hammond mechanism. The dependence upon trialkylamine concentration is surprising, however, as shown by the data plotted in Fig. 1, where initial rates are plotted against the inverse square root of the inhibitor concentration. In all cases, the substrate was 4 M cumene in chlorobenzene with 4×10^{-3} M AIBN as initiator.

The surprising feature of the data is the fact that at high concentrations the rate becomes essentially independent of amine concentration. This behavior is not due to a reduction of the kinetic chain length to near one as can be demonstrated by the fact that diphenylamine at modest concentration (10^{-3} M) reduces the rate by more than an additional order of magnitude.

The only mechanism, apparent to us, to explain the observed behavior is an extension of the charge-transfer complex postulate. This mechanism, which is outlined below, contains the normal Boozer–Hammond sequence, (3) and (4), but also allows for chain propagation by the complex species (5) and bimolecular com-

(1) G. Dixon-Lewis and J. W. Linnett, *Proc. Roy. Soc.* (London), **A210**, 48 (1951).
(2) D. J. Waddington, *ibid.*, **A265**, 436 (1962).
(3) C. E. Boozer and G. S. Hammond, *J. Am. Chem. Soc.*, **76**, 3861 (1954).
(4) J. R. Thomas and C. A. Tolman, *ibid.*, **84**, 2930 (1962).
(5) J. R. Thomas, *ibid.*, **85**, 591 (1963).