and the hydroxylic component of the mixtures on the products of the solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate will be reported.

Experimental Section

Materials and Methods. Equipment has been previously described.[13] Use was made of 6-ft columns of 20% Carbowax 20M on Chromosorb P. Melting points are corrected and boiling points are uncorrected.

Solvents and reagents were usually commercial materials which were purified by distillation or recrystallization if necessary. *p*-Methylanisole was prepared from the corresponding phenol and dimethyl sulfate.[14] Ethyl stearate was prepared from stearic acid and ethanol.[15] Acetates were prepared by standard methods.

Product Studies. To weighed quantities of the *p*-nitrobenzenesulfonate and urea was added 1.00 ml of acetic acid and 4.00 ml of inert solvent, if it was a liquid at room temperature. When necessary the mixture was warmed slightly to help make it homogeneous and transferred to a constricted tube which was then sealed at atmospheric pressure. After the mixture was heated for a definite period of time, the mixture was cooled and the tube was opened. A measured amount (*ca.* 17 mg) of an internal standard (pentyl acetate),[16] ether, and saturated sodium chloride solution were added, and the ether layer was separated after shaking and washed with saturated sodium chloride solution and saturated sodium bicarbonate solution. The volume of ether was kept small so that no concentration step was necessary prior to glpc analysis. The ethereal solution was dried over anhydrous magnesium sulfate and then passed through a cotton filter into a sample vial. Prior to glpc analysis approximately 0.2 g of anhydrous magnesium sulfate was added to the sample vial to ensure dryness.[17]

If the inert solvent was a solid at room temperature, a weighed quantity equivalent to 4.0 ml of the solid was placed in the constricted tube and the acetic acid solution of the substrate and base was added to the tube. The mixture was treated as above except that after the standard was added, the solid solution plus the tube was placed in a flask fitted with a reflux condenser. Ether was added, and the mixture was heated to reflux for at least 1 hr. After cooling, the ether solution was decanted into a separatory funnel, and the residue was washed four times with ether. The ether solutions were combined and treated as described above.

The yields of the products were determined by glpc. The areas of the product peaks were compared to the area of the standard peak, and the absolute yields of the products based on the average of at least three glpc traces were determined by use of experimentally determined relative thermal conductivity and extraction ratios. Average values for three determinations of the relative thermal conductivity and extraction ratios to pentyl acetate were found to be 0.690 for cyclohexene, 1.400 for hexyl acetate, 1.155 for 5-hexenyl acetate, and 0.894 for cyclohexyl acetate. It was found that these ratios were very close to experimentally determined relative thermal conductivities and thus the relative extraction ratios are *ca.* 1.0. It was also found that these ratios were the same within 2% for extraction from acetic acid, nitrobenzene, and sulfolane. Since these three solvents are very different, it was assumed that these ratios did not vary from mixture to mixture.

Measurement of *Z* values was patterned after the method of Kosower.[12]

Acknowledgment. This study was initiated in the laboratory of Professor Paul D. Bartlett whom we thank for encouragement. We are grateful for some preliminary work by Mr. Tony Chiu,[1d] the measurement of the *Z* values by Richard E. Ehlers, the preparation of some compounds by L. Brewster Young, and an informative discussion with Professor C. D. Ritchie. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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[13] W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, 32, 146 (1967).

[14] G. S. Hiers and F. D. Hager, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 58.

[15] S. Natelson and S. Gottfried, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 381.

[16] The internal standard was hexyl acetate when tri-*n*-amyl borate was used as the inert solvent.

[17] Without inclusion of this last step, quantitative glpc analysis was almost impossible in some solvent mixtures.

Chain Termination *via* Cumylperoxy Radicals

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Abstract: It is pointed out that the yield of acetophenone per reaction chain initiated in the autoxidation of cumene, or in the chain decomposition of cumene hydroperoxide, can exceed the value of 0.5 which is required by a reaction scheme recently proposed by Traylor and Russell.[1] In the initiated chain decomposition of cumene hydroperoxide at 57°, it is found that the chain length reaches a constant value at considerably lower cumene hydroperoxide concentrations than that required for suppression of acetophenone formation. This behavior can be rationalized if the chain-terminating reactions of methylperoxy radicals are sufficiently slow that under many conditions methylperoxy radicals effectively continue chain propagation.

Recently Traylor and Russell[1] presented convincing arguments that an important chain-terminating reaction in the autoxidation of cumene involved production of methyl radicals by *β* scission of cumyloxy radicals with subsequent fast termination by reaction of methylperoxy with cumylperoxy radicals. In reducing their ideas to quantitative terms, these authors relied heavily upon the work of Blanchard,[2] who first determined the yield of acetophenone in the oxidation of cumene and thus demonstrated the potential importance of *β* scission of cumyloxy radicals in the oxidation reaction. The mechanism of Traylor and Russell calls for a maximum yield of one acetophenone per chain-terminating reaction (destruction of two chain-carrying radicals), and they cited Blanchard's results in confirmation of their ideas. Unfortunately, an error of a factor of two was made in transcribing Blanchard's data, which were reported in two sets of units. Under the conditions of his experiments, Blanchard found an

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[1] T. G. Traylor and C. A. Russell, *J. Am. Chem. Soc.*, 87, 3698 (1965).

[2] H. S. Blanchard, *ibid.*, 81, 4548 (1959).

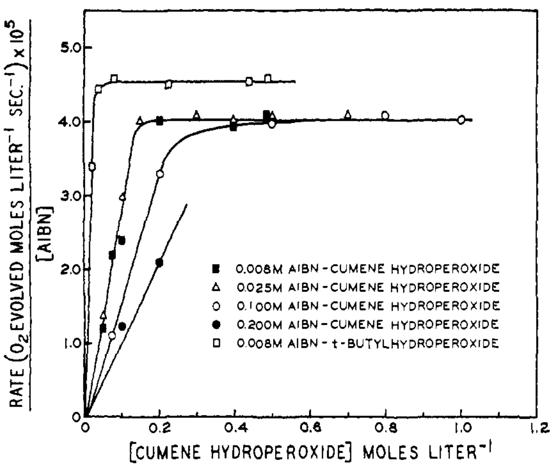

Figure 1. Rate of oxygen evolution/[AIBN] *vs.* cumene hydroperoxide concentration; 57.2°, chlorobenzene diluent, 1 atm of O_2.

average of 1.4 acetophenones per chain-termination reaction rather than 0.7 as quoted by Traylor and Russell, which reopens the question of the detailed chemistry of the termination reaction.

In this paper, data are presented which suggest that methylperoxy termination reactions are sufficiently slow relative to transfer reactions that under many conditions these radicals continue to propagate reaction chains. The experiments involve the influence of cumene hydroperoxide, a scavenger for cumyloxy radical, upon the yield of acetophenone and upon the rates of oxidation of cumene and the chain decomposition of the hydroperoxide.

Experimental Section

Materials. Cumene hydroperoxide was purified three times *via* the sodium salt. Each preparation was checked for absence of inhibiting trace contaminants by monitoring its effect at 0.1 *M* on the AIBN (azobisisobutyronitrile) catalyzed oxidation of 3.6 *M* cumene in chlorobenzene. *t*-Butyl hydroperoxide was purified by fractional crystallization. Both Eastman and Phillips research grade cumene were used after treatment with activated alumina. The source of the material did not influence the results. AIBN was recrystallized from methanol. Eastman chlorobenzene was treated with activated alumina.

Kinetic Studies. The rates of oxidation of cumene and oxygen evolution during the chain decomposition of the hydroperoxide were determined as reported previously.[3]

Acetophenone Yield. The method of Blanchard[2] was used to determine the yield of acetophenone.

Results and Discussion

In Figure 1 the oxygen evolution rate during the AIBN-induced decomposition of cumene hydroperoxide is plotted against hydroperoxide concentration for several AIBN concentrations. As noted there, this rate becomes independent of hydroperoxide concentration at values greater than several tenths molar, in agreement with previously reported work.[4–6] The rate of approach to this situation is somewhat dependent upon the AIBN concentration at higher concentrations, however. This could arise from termination involving AIBN–peroxy radicals or by participation of cumyloxy radicals directly in termination. Both reactions will be favored by higher initiation rates. However, since with *t*-butyl hydroperoxide, also shown in Figure 1, the effect of its concentration saturates considerably sooner than with cumene hydroperoxide, it seems reasonable to assign the behavior at low AIBN concentrations shown in Figure 1 to processes resulting from β scission of cumyloxy radicals. In the analysis to follow, the approach to saturation at AIBN concentrations of both 0.008 and 0.1 *M* will be treated as arising from the β-scission process, but it should be kept in mind that this is strictly true only for the lower level. Since the peroxy radical abstraction rate of hydrogen from hydroperoxide is several orders of magnitude greater than that from cumene, the possibility of incomplete AIBN–peroxy radical trapping at high initiation rates (equal to or greater than that corresponding to 0.1 *M* AIBN at 57°), with cumene concentrations of several molar or less, should be kept in mind.

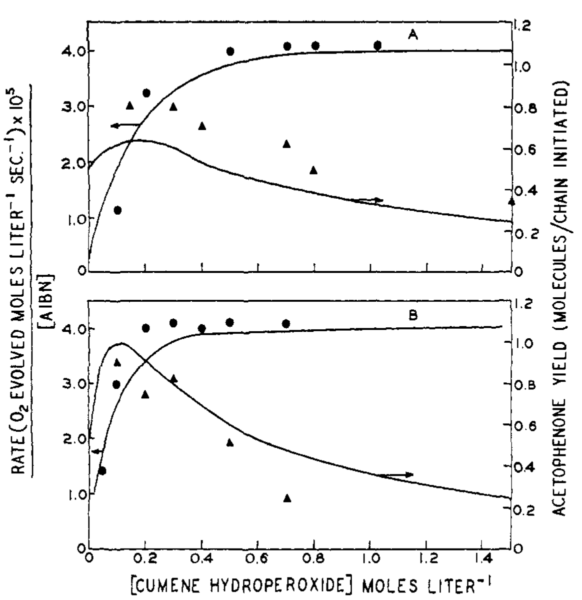

Figure 2. Rate of oxygen evolution/[AIBN] and acetophenone yield *vs.* cumene hydroperoxide concentration. Solid curves are theoretical; 57.2°F, chlorobenzene diluent, A = 0.1 *M* AIBN, B = 0.008 *M* AIBN.

In Figure 2 the oxygen evolution rate data at 0.008 and 0.1 *M* AIBN are given again together with acetophenone yield data, both as a function of hydroperoxide concentration. Note that the acetophenone yield is given as molecules of acetophenone per chain initiated. The solid curves are calculated as discussed below.

By Traylor and Russell's view of the termination reaction in cumene, it would be expected that the chain length of hydroperoxide decomposition would *increase* continuously until such time as the acetophenone yield was reduced to near zero. As can be seen from Figure 2, the chain length becomes constant at hydroperoxide concentrations of several tenths molar where the acetophenone yield is still about 0.8 molecule per chain or about 1.6 molecules per terminating reaction. Consequently, it might be concluded that every methyl radical produced in the β-scission reaction does not necessarily lead to termination. It would appear that hydroperoxide scavenges the methylperoxy radical as well as the cumyloxy radical and that the saturation point in plots such as Figures 1 and 2 corresponds to almost complete

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(5) A. Factor, C. A. Russell, and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3692 (1965).

(6) J. R. Thomas, *ibid.*, **87**, 3935 (1965).

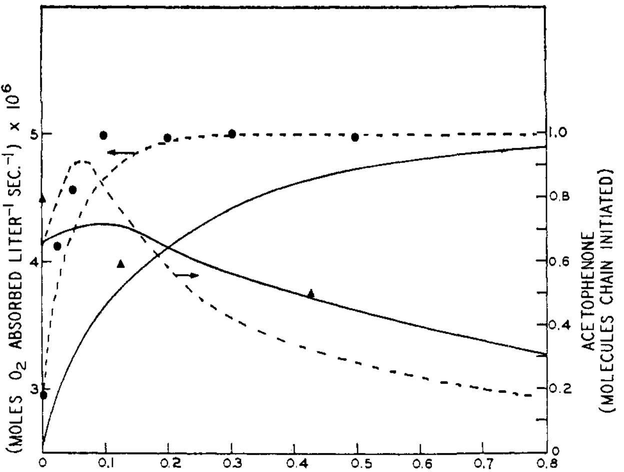

Figure 3. Oxidation rate and acetophenone yield of 3.6 *M* cumene *vs.* cumene hydroperoxide concentration. Solid curves are theoretical; 57.2°, chlorobenzene diluent, 0.008 *M* AIBN, 1 atm of O_2, - - - -, calculated with $k_p/k_f = 60$ l. mole^{-1}, $k_p'/k_t = 10^{-4}$; ———, calculated with $k_p/k_f = 30$ l. mole^{-1}, $k_p'/k_t = 10^{-5}$; ●, experimental oxygen absorbtion rate; ▲, experimental acetophenone yield.

scavenging of the former radical rather than the latter radical.

The situation outlined above can be expressed in terms of the following mechanism where $RO_2\cdot$ designates cumylperoxy radical and R_i is the AIBN initiation rate.

$$\begin{array}{lr}
\text{AIBN} \xrightarrow{O_2} RO_2\cdot & R_i \\
RO_2\cdot + RO_2\cdot \longrightarrow 2RO\cdot + O_2 & k_1 \\
RO\cdot \xrightarrow{O_2} CH_3O_2\cdot + CH_3COC_6H_5 & k_f \\
RO\cdot + ROOH \longrightarrow RO_2\cdot + ROH & k_p \\
CH_3O_2\cdot + ROOH \longrightarrow RO_2\cdot + CH_3O_2H & k_p' \\
RO_2\cdot + CH_3O_2\cdot \longrightarrow X & k_t \\
RO_2\cdot + RO_2\cdot \longrightarrow ROOR + O_2 & k_2
\end{array}$$

This mechanism yields the steady-state expression 1 for the cumylperoxy radical concentration. The solid curves in Figure 2 were calculated from derived cumylperoxy radical concentrations by eq 1 and the subsequently easily obtained cumyloxy radical concentration. The

$$R_i = \frac{4k_1[RO_2\cdot]^3}{\left(\frac{k_p}{k_f}[ROOH] + 1\right)\left(\frac{k_p'}{k_t}[ROOH] + [RO_2\cdot]\right)} + 2k_2[RO_2\cdot]^2 \quad (1)$$

oxygen evolution rate function of Figure 2 was calculated by considering only reactions 1 and 2 as shown in eq 2. The calculations were made with $k_1 = 3.85 \times 10^5$ and $k_2 = 4.05 \times 10^4$ l./mole sec. These values were chosen to give the correct ratio of k_1/k_2 as defined by the high hydroperoxide concentration limiting value.

Limiting rate of oxygen evolution =

$$(k_1 + k_2)[RO_2\cdot]^2 = (k_1 + k_2)\frac{R_i}{2k_2} \quad (2)$$

or

$$\frac{\text{limiting rate}}{[\text{AIBN}]} = \frac{k_i}{2}\left(\frac{k_1}{k_2} + 1\right)$$

The absolute value of k_2 was picked as a reasonable value,[7] while k_i is the rate constant defining chain initiation by AIBN at this temperature and has the value 7.7×10^{-6} sec^{-1}. The quantities k_p/k_f and k_p'/k_t are unknowns whose values are to be selected to give fit to the experimental data. It proved easiest, and satisfactory for our purposes, to fit the two responses separately. Modest optimization of the oxygen evolution data at the two AIBN concentrations gave $k_p/k_f = 41.8$ l. mole^{-1} and $k_p'/k_t = 10^{-4.3}$. Separate treatment of the acetophenone yield data gave $k_p/k_f = 23.6$ l. mole^{-1} and $k_p'/k_t = 10^{-5.0}$. Our purpose here is not to determine these values with high accuracy but rather to see if their order of magnitude is such that the above mechanism can be offered as a plausible explanation for the experimental observations.

From the data of Walling and Wagner[8] and Walling and Jacknow,[9] a value of k_p/k_f for abstraction of hydrogen from cumene of approximately 0.7 l. mole^{-1} can be estimated. The considerably higher value of this quantity for the hydroperoxide noted above is consistent with our current knowledge. The absolute value for abstraction of hydrogen from tetralin hydroperoxide by cumylperoxy radical has been estimated[10,11] to be as high as 10^2 l. mole^{-1} sec^{-1}, which implies that k_t must be the order of 10^7 l. mole^{-1} sec^{-1}, a not unreasonable value.

As mentioned earlier, some bias has been incorporated into the parameters k_p/k_f and k_p'/k_t by attributing all of the rise-to-saturation effect at 0.1 *M* AIBN to the steps outlined in the above mechanism. As the calculated curves in Figure 2 show, however, this mechanism is not very sensitive to AIBN concentration, and the effect of this bias should be slight.

When cumene hydroperoxide is added to autoxidizing cumene, the oxidation rate is accelerated as first reported by Traylor and Russell.[1] The magnitude of the effect observed in this work was somewhat less than that observed by Traylor and Russell, and, perhaps more importantly, the effect saturates much sooner than that reported by these authors. As the effect was quite independent of the source of materials, and very reproducible, we believe it to be correct. In Figure 3 oxidation rate data and acetophenone yield data at 0.008 *M* AIBN for 3.6 *M* cumene are plotted as a function of cumene hydroperoxide concentration. A slightly slower rate of saturation was observed at 0.1 *M* AIBN, but the various uncertainties such as the oxygen evolution correction and initiator inefficiency render the data less useful. The solid curves in Figure 3 were calculated using an appropriate modification of eq 1 to allow for reaction of cumyloxy and methylperoxy with cumene as well as hydroperoxide. Little attempt was made to adjust parameters for best fit except that the propagation rate constant for peroxy radicals was chosen as 1.61 l. mole^{-1} sec^{-1} (compared to a best value[7] of 0.8 mole^{-1} sec^{-1}) in order to fit the calculated saturation rate with the experimental value using the known initiation rate and the previously selected value of k_2. The other parameters chosen (one trial with $k_p/k_f = 30$ l. mole^{-1}, $k_p'/k_t = 10^{-5}$ (both for hydroperoxide); a second with

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(7) K. U. Ingold, private communication.

(8) C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964).

(9) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6108 (1960).

(10) J. R. Thomas and C. A. Tolman, *ibid.*, **84**, 2079 (1962).

(11) Early work[10] yielded a value of about 10 l. mole^{-1} but recent work using a different technique suggests a somewhat higher value.

60 and 10^{-4}, respectively; and $k_p/k_f = 0.7$ l mole^{-1}, $k_p'/k_t = 10^{-7}$ (both for cumene)) were picked as reasonable values in light of the previous discussion. Again the attempt here is solely to demonstrate that the mechanism offers a plausible semiquantitative explanation of the results.

In summary, these results confirm Traylor and Russell's thought that methylperoxy radicals contribute significantly to chain termination in the oxidation of cumene under most conditions. The acceleration in rate observed in the presence of moderate concentrations of cumene hydroperoxide, however, appears due primarily to trapping of methylperoxy radicals rather than cumyloxy radicals.

Acknowledgment. The author is indebted to Mr. L. J. Painter for the computer calculations.

The Succinimidyl Radical Problem. The Ease of Formation of Nitrogen and Oxygen Π and Σ Free Radicals

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Tarrytown, New York 10591. *Received April 25, 1967*

Abstract: The syntheses of two potential sources of the succinimidyl radical, N,N′-bisuccinimide and *t*-butyl N-succinimidepercarboxylate, are described. The bisuccinimide, it turns out, had been obtained previously by dehydrating a 2:1 mixture of succinic acid and hydrazine but identified as an isomeric six-membered ring structure, 1,4,6,9-tetraketopyridazo[1,2-*a*]pyridazine. An unequivocal chemical proof of structure for N,N′-bisuccinimide was carried out; it involves the synthesis and proof of structure for the six-membered ring isomer, which rearranges to N,N′-bisuccinimide both in dioxane solvent and on melting. N,N′-Bisuccinimide itself is highly stable; it was recovered unchanged from a variety of extreme decomposition conditions. Consistently, *t*-butyl N-succinimidepercarboxylate is more stable toward homolytic decomposition in chlorobenzene than *t*-butyl percarbamate. The former peroxide decomposed mainly by way of a heterolytic Criegee rearrangement, but predominant homolysis could be induced by photolysis in cumene or toluene leading to high yields of succinimide and coupling products derived from the solvent. It is concluded that these results strongly imply an N–N dissociation energy D for N,N′-bisuccinimide of 50 kcal or more rather than a facile reversible dissociation to stable radicals that do not subsequently follow any substantially irreversible path. The general problem of the ease of formation of nitrogen radicals, primarily from hydrazines bearing potentially conjugating substituents, is considered in terms of the energy differences between Σ and Π states for a particular nitrogen radical and between planar and angular dimers, as well as 1- and 2-electron π conjugation in the radical and dimer and the effects of sp hybridization on orbital and bond energies. Four extreme cases of dissociation are recognized: angular dimer to Π radicals, planar dimer to Σ radicals, angular dimer to Σ radicals, and planar dimer to Π radicals. For the first, D is approximately the standard dissociation energy $D°$ (hydrazine) less twice the one-electron conjugation energy of the radicals; for the second, D is essentially $D°$ plus an increment, B, due to hybridization; and for the fourth, D is equal to $D° + B$, the planar-to-Σ dissociation energy, less twice the Σ–Π energy difference in the radical. The third case is shown to be impossible for ground-state radicals and dimers. It is then suggested that D is high for N,N′-bisuccinimide because the planar dimer dissociates to Σ radicals as seems probable from simple molecular orbital theory, which shows that the Σ–Π energy differences for succinimidyl and acylamino must be less than for vinylamino, or even negative. Correspondingly, D should be *low* for the vinylamino dimer. The molecular orbital results are summarized for radicals having the triad structure R—C(=B)A (A, B = CH_2, NH, or O; A $\neq$ CH_2) in terms of the electronegativities of A and B. In general, as B becomes increasingly more electronegative than A, the Σ–Π energy difference and the ease of dissociation of the dimer decrease. The dissociations of aryl-, vinyl-, and acyl-substituted hydrazines, amines, peroxides, and alcohols to give the corresponding nitrogen and oxygen radicals are discussed on the basis of this model.

Succinimidyl radical has not been unequivocally characterized, despite frequent mention in the literature including predictions of high stability corresponding to estimated resonance energies of 17[2] to 30 kcal/mole.[3] In the recent reinterpretation[4] of the mechanism of the N-bromosuccinimide (NBS) bromination of hydrocarbons (Wohl–Ziegler reaction) the bromine atom has replaced it as chain propagator, but it remains as a plausible radical intermediate in the radical-induced rearrangement of NBS to β-bromopropionyl isocyanate[5] and in the formation of addition products with olefins.[6] The former reaction appears

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[1] To whom inquiries should be addressed.

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