

of allyl-1- d_2 acetate. The mixture was heated at gentle reflux for 90 min.; at which time a starch iodide test indicated complete reaction of the *N*-bromobenzamide. On being set aside overnight in a refrigerator, 0.89 g. of crude benzamide (m.p. 115–120°) deposited from solution. A single recrystallization from benzene (Norite) gave 0.6 g. (39.8%) of pure benzamide, m.p. 127°. The infrared spectrum (CHCl_3) was identical with that of nondeuterated benzamide and showed no absorption at 4.2μ .

Benzamide-N,N-d_2. A mixture of 0.9 g. of sodium benzamide and 3 ml. of deuterium oxide (99.8% isotropically pure) was warmed until a clear solution was obtained. The solution was protected from atmospheric moisture and allowed to crystallize. The benzamide-*N,N-d_2* which deposited was isolated by filtration and dried *in vacuo*, m.p. 123–124°. One recrystallization from benzene gave 0.38 g.

(50%) benzamide-*N,N-d_2*, m.p. 127°. Infrared spectrum (see Fig. 1) shows absorption at 3.9–4.3 μ , N—D,¹⁷ absent in the spectrum of ordinary benzamide. It is very likely that benzamide-*N,N-d_2* rather than *N*-deuterobenzamide was formed in this preparation since the work of Brodskii¹⁸ some years ago showed that amide hydrogen atoms exchange readily with the hydrogens of water, even in the absence of a catalyst. In the present case, by-product deuterated sodium hydroxide would be expected to catalyze the exchange of all amide hydrogen atoms in benzamide. However, the use of either the mono or di deuterio benzamide would not alter the conclusions arrived at in the present investigation.

EAST LANSING, MICH.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

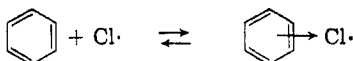
Solvent Effects in the Reaction of Free Radicals and Atoms. V. Effects of Solvents on the Reactivity of *t*-Butoxy Radicals

GLEN A. RUSSELL¹

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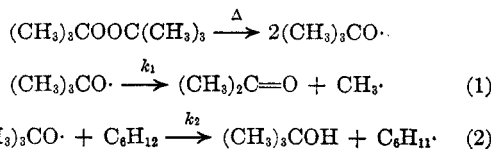
The effects of solvents upon the products of decomposition of di-*t*-butyl peroxide at 130° are considered. Quantitative data in regard to the peroxide-catalyzed reaction of chloromethanes with cyclohexane are presented. Evidence is presented supporting the displacement of a chlorine atom from 1-chloronaphthalene by a *t*-butoxy radical.

Previous papers in this series have demonstrated that aromatic solvents can drastically alter the reactivity of a chlorine atom.² These results have been interpreted in terms of a π -complex formed between the electrophilic chlorine atom and the electron-donating aromatic nucleus.



The complexed chlorine atom is apparently less reactive and more selective in its reactions than the free chlorine atom. Since *t*-butoxy radicals have a reactivity quite similar to chlorine atoms,³ it was of interest to ascertain if similar solvent effects could be detected in the reactions of these radicals.

Solvent effects have been investigated in the decomposition of di-*t*-butyl peroxide in the presence of cyclohexane at 130° by measuring the fraction of *t*-butoxy radicals which enter into the decomposition reaction (1) and the hydrogen-abstraction reaction (2). From the ratio of acetone and *t*-



(1) Present address, Dept. of Chemistry, Iowa State College, Ames, Iowa.

(2) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 2977 (1957); **80**, 4987, 4997, 5002 (1958).

(3) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

butyl alcohol formed it is possible to calculate the ratio of k_1/k_2 provided that the products do not result from radical-radical interaction and provided that acetone and *t*-butyl alcohol are formed only in reactions 1 and 2. The former requirement will always be satisfied when the ratio of acetone and *t*-butyl alcohol is independent of *t*-butoxy radical concentration, while the latter requirement will nearly always be satisfied when the combined yield of acetone and *t*-butyl alcohol is quantitative based on the starting di-*t*-butyl peroxide. Table I presents data wherein these requirements have been met.

The ratio of k_1/k_2 is 0.45–0.47 when cyclohexane or methylene chloride are used as solvents. The same ratio is observed when the weakly basic benzotrifluoride is used as a solvent. For more basic aromatic solvents, such as benzene, chlorobenzene or diphenyl ether, higher values of k_1/k_2 are observed although the highest value observed is only 25% greater than the value observed in an aliphatic solvent. However, the increase in the ratio of k_1/k_2 is considerably above experimental uncertainty.

The possibility that hydrogen abstraction from the aromatic solvent could occur to a significant extent is easily eliminated. Aromatic solvents cause an increase in the ratio k_1/k_2 whereas production of *t*-butyl alcohol by abstraction of a hydrogen atom from the aromatic solvent would lead to a decrease in this ratio. Moreover, estimates of the relative reactivities of cyclohexane and benzene toward a *t*-butoxy radical have been reported by Williams,

TABLE I
 PRODUCTS OF THE DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE AT 130°

Solvent	Solvent Conc. ^a	C ₆ H ₁₂ ^a	Me ₃ COOCMe ₃ ^a	Products, mmol. ^b		Yield of acetone and <i>t</i> -butyl alcohol ^b	<i>k</i> ₁ / <i>k</i> ₂ ^c
				Me ₃ COH	Me ₂ C=O		
C ₆ H ₁₂	7.84	7.84	0.0926	5.30	0.310	103	0.46
C ₆ H ₁₂	7.84	7.84	.0463	5.25	.305	102	.45
CH ₂ Cl ₂	7.95	2.98	.0934	4.77 ^d	.745	101	.47
C ₆ H ₆	5.81	3.00	.0936	4.65	.849	101	.55
C ₆ H ₅ Cl	4.45	3.04	.0954	4.60	.940	101	.60
C ₆ H ₅ CF ₃	4.05	2.94	.0924	4.85	.750	103	.47
C ₆ H ₅ OC ₆ H ₅	3.28	3.04	.0954	4.30	.788	94	.56
1-Chloronaphthalene	3.40	3.16	.0990	4.27 ^e	.338	85	—

^a Mole/liter. ^b On the basis of 2.725 mmol. of di-*t*-butyl peroxide. ^c $\frac{k_1}{k_2[C_6H_{12}]} = \frac{\text{acetone}}{t\text{-butyl alcohol}}$. ^d Sum of *t*-butyl alcohol, *t*-butyl chloride and isobutylene, see Table II. ^e 3.54 mmol. *t*-butyl alcohol, 0.355 mmol. *t*-butyl chloride, 0.370 mmol. isobutylene.

Oberright, and Brooks.⁴ At 135° these workers found that a hydrogen atom of benzene was only about 1/700 as reactive as a hydrogen atom of cyclohexane. For the experiments summarized in Table I the concentration of aromatic hydrogen atoms was usually less than the concentration of cyclohexane hydrogen atoms and thus it can be safely assumed that only about 1 part per 1000 of the *t*-butyl alcohol could have been formed from the interaction of *t*-butoxy radicals with the aromatic solvent.

Aromatic solvents appear to favor the decomposition of *t*-butoxy radicals relative to hydrogen abstraction from cyclohexane. The relative effectiveness of aromatic solvents of C₆H₅OC₆H₅, C₆H₅Cl, C₆H₅>C₆H₅CF₃ is qualitatively in agreement with the results observed in the photochemical chlorination of branched-chain hydrocarbons.² However, the solvent effect in the reactions of *t*-butoxy radicals at 130° is considerably less than the solvent effect noted in photochlorinations at 20–55°.² There are several possible explanations to the differences in the magnitude of the solvent effect observed in these reactions. The temperature employed in the present work (130°) may be so high that the aromatic hydrocarbon-*t*-butoxy radical π -complex is extensively dissociated. Moreover, the driving force for the formation of this complex may be considerably less for a *t*-butoxy radical than a chlorine atom since the desire of a *t*-butoxy radical for an electron is considerably less than that of a chlorine atom. Expressed in terms of electron affinity the reaction of a chlorine atom with an electron is exothermic to the extent of 88 kcal./mole while the similar reaction for an alkoxy radical is exothermic only to the extent of about 50 kcal./mole.⁵ Because of this a *t*-butoxy

radical may be expected to form a weaker π -complex with benzene than a chlorine atom. Finally, a solvent may affect both reactions 1 and 2 to the same degree and thus partially obscure an experimental demonstration of the solvent effect from a study of competitive reaction rates.

Two experimental values for *k*₁/*k*₂ in cyclohexane have been previously reported, 0.855 (135°)⁶ and 0.435 (135°).⁴ Using a difference in energy of activation for reactions 1 and 2 of 6.5 kcal./mole⁶ the ratio of *k*₁/*k*₂ is calculated to be 0.77 (130°)⁶ and 0.39 (130°).⁴ The experimentally determined value of 0.46 reported in the present work is intermediate between the two previously determined values but is much closer to the lowest of these values.

The decomposition of di-*t*-butyl peroxide in the presence of mixtures of cyclohexane and chloroform or carbon tetrachloride were also quantitatively investigated. Here the decomposition is complicated by the occurrence of a chain reaction between the chloromethane and cyclohexane.⁷

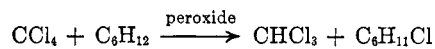


Table II summarizes the products formed in the reaction of the chloromethanes and cyclohexane at 130°.

Kinetic chain lengths for the chlorination reaction were about 16 for carbon tetrachloride, 1 for chloroform and <0.15 for methylene chloride. Undoubtedly this is in indication of the reactivity of the carbon-chlorine bonds in these molecules toward an alkyl radical and results from the relative stability of the chloroalkyl radicals of CCl₃· > CHCl₂· > CH₂Cl·.

In the reaction of carbon tetrachloride with cyclohexane all products more volatile than chlorocyclohexane were analyzed. The material balance

(4) A. L. Williams, E. A. Oberright, and J. W. Brooks, *J. Am. Chem. Soc.*, **78**, 1170 (1956).

(5) H. O. Prichard, *Chem. Revs.*, **52**, 529 (1953) reports the electron affinity of a hydroxyl radical to be 50 kcal./mole.

(6) J. H. T. Brook, *Trans. Faraday Soc.*, **53**, 327 (1957).

(7) J. P. West and L. Schmerling, *J. Am. Chem. Soc.*, **72**, 3525 (1950).

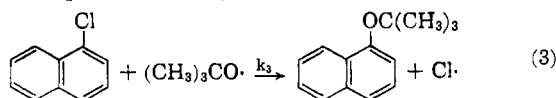
TABLE II
PRODUCTS OF THE REACTION OF CHLOROMETHANES AND
CYCLOHEXANE AT 130°

Reactants	Quantities, mmole		
CH ₂ Cl ₂	—	—	93.0
CHCl ₃	—	74.4	—
CCL ₄	67.0	—	—
C ₆ H ₁₂	34.8	34.8	34.8
Me ₃ COOCMe ₂	1.09	1.09	1.09
Products			
CH ₃ Cl	0.29	0.30	0.30
CH ₂ Cl ₂	0.07	2.50	93.
CHCl ₃	35.5	72.0	0.15
CCL ₄	31.3	—	—
C ₆ H ₁₂	8.3	30.5	33.7
C ₆ H ₁₁ Cl	18.6	1.10	<0.10
Me ₃ COH	0.58	0.67	1.12
Me ₂ CCl	.20	.27	.05
Me ₂ C=CH ₂	.70	.81	.74
Me ₂ CO	.29	.27	.30

indicates that 17.1 mmol. of chlorine and 7.9 mmol. of C₆ fragments are unaccounted for, while an excess of hydrogen (on the basis of chlorocyclohexane found) of 17.6 mmol. was found in the volatile products. These results suggest that 8–9 mmol. of a dichlorocyclohexane was formed in addition to the 18.6 mmol. of chlorocyclohexane.

Significant amounts of *t*-butyl chloride were found in the decomposition of di-*t*-butyl peroxide in the presence of chloromethane–cyclohexane mixtures. Isobutylene was also formed although it could not be detected in the absence of the chloroalkane. This suggests that hydrogen chloride is formed in the presence of the chloroalkane and that in its presence *t*-butyl alcohol is in part dehydrated and in part converted to *t*-butyl chloride. In a trial experiment it was found that at 130° chlorocyclohexane did not bring about the dehydration of the alcohol or the formation of a detectable amount of *t*-butyl chloride. Possibly, the *t*-butoxy radical can abstract a chlorine atom from the chloromethane to yield *t*-butyl hypochlorite which would thermally decompose yielding a chlorine atom.

Isobutylene and *t*-butyl chloride were also formed in the decomposition of di-*t*-butyl peroxide in the presence of 1-chloronaphthalene but not in the presence of chlorobenzene. Moreover, the combined yield of acetone and *t*-butyl alcohol accounted for only 85% of the di-*t*-butyl peroxide employed in the presence of 1-chloronaphthalene whereas these products accounted for 101% of the peroxide in the presence of chlorobenzene. These results suggest that *t*-butoxy radicals can react with 1-chloronaphthalene to yield chlorine atoms.



Similar reactions, not involving alkoxy radicals, have been described by Miller and Walling.⁸

Chloronaphthalene is apparently much more reactive than chlorobenzene in this reaction, a fact consistent with the greater reactivity of naphthalene derivatives than benzene derivatives in most aromatic substitutions. From the amount of *t*-butyl chloride formed in the presence of 1-chloronaphthalene (see Table I) it is calculated that the ratio of k_3/k_2 is 0.08. If 0.36 mmol. of *t*-butoxynaphthalene is formed, as indicated by the formation of 0.36 mmol. of *t*-butyl chloride, then the yield of di-*t*-butyl peroxide fragments in the experiment summarized in Table I accounts for 94% of the peroxide used. It now seems valid to calculate a value for the ratio k_1/k_2 in the presence of chloronaphthalene on the basis of acetone, *t*-butyl alcohol, *t*-butyl chloride, and isobutylene formed. This calculation indicates a value of 0.25 for k_1/k_2 , whereas on the basis of basicity of solvent we might have expected aromatic solvents to have solvent effects in the order chloronaphthalene > diphenyl ether > benzene > chlorobenzene > benzotrifluoride.² However, 1-chloronaphthalene may effect the products of the reaction in a more profound manner than has been indicated. The *t*-butylnaphthyl ether may be cleared by hydrogen chloride to yield the *t*-butyl chloride observed. Moreover, the possibility exists that *t*-butoxy radicals may abstract hydrogen atoms from the naphthalene nucleus or add to the nucleus to give an unstable intermediate capable of decomposition to *t*-butyl alcohol

EXPERIMENTAL

A standard solution of di-*t*-butyl peroxide in Phillips reagent grade cyclohexane was weighed into a volumetric flask and diluted with a weighed amount of purified solvent. An aliquot of this solution was added to an ampoule prepared from a 1 ml. Mohr pipette calibrated in 0.01 ml. divisions. The solution was degassed and the ampoule sealed at reduced pressure. The concentration of reactants at 130° was obtained from their known concentrations at 25° by applying a correction for the observed volume change observed between 25 and 130° by using the calibrated reaction ampoule.

The ampoule was held at 130° in an oil-bath for 48 hr. This period represents approximately 10 half-lives for the peroxide and should have resulted in the decomposition of 99.9% of the peroxide. After this period the ampoule was opened at liquid nitrogen temperature and a sample injected into a Perkin-Elmer model 154B Vapor Fractometer.

The ratio of acetone, *t*-butyl alcohol, *t*-butyl chloride, isobutylene, and cyclohexane was determined from the appropriate peak areas using experimentally determined calibration curves. Usually it was assumed that the quantity of cyclohexane in the reactants and products was essentially constant. In experiments employing carbon tetrachloride or chloroform this assumption was not valid and analysis was based on the fact that the quantity of carbon tetrachloride or chloroform in the reactants should be very nearly equal to the sum of the quantities of carbon tetrachloride, chloroform, and methylene chloride in the products.

SCHENECTADY, N. Y.

(8) B. Miller and C. Walling, *J. Am. Chem. Soc.*, **79**, 4187 (1957).