Thermal Decomposition of Allyl-*t*-butylperoxide.—Allyl-*t*-butylperoxide (7.0 g.) was heated for 72 hours at 60°, then the products distilled. The distillate, which all distilled below 85° at 760 mm., weighed 4.60 g. and reeked of acrolein. A polymeric residue (2.15 g.) remained in the distilling flask; this residue may be principally acrolein polymer. A sample of the distillate was hydrogenated over Adams catalyst; from the data, it was calculated that the distillate was about 25% acrolein and 75% *t*-butyl alcohol. From 1.0 g. of distillate, hydrogenated in ethanol, was obtained 0.8 g. of propionaldehyde 2,4-dinitrophenylhydrazone (about 90%). Final confirmation of the composition of the distillate was made by comparing its infrared spectrum with that of a synthetic sample of 25% acrolein and 75% *t*-butyl alcohol. From these data it appears that the decomposition of allyl-*t*-butylperoxide to acrolein and *t*-butyl alcohol is smooth and nearly quantitative. Formaldehyde was looked for carefully and could not be found among the decomposition products.

Cyclohexenyl-*t*-butylperoxide.—This compound was made as above, with the substitution of 92 g. of 3-bromocyclohexene for the allyl bromide. The product, obtained in 45% yield, was a pleasant-smelling oil, b.p. 63° (6 mm.).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.6; H, 10.6. Found: C, 70.4; H, 10.7.

Decomposition of Cyclohexenyl-*t*-butylperoxide.—The peroxide (4.0 g.) was heated slowly at 760 mm. to boiling and held there 30 minutes. Decomposition was smooth. The product was distilled up to 160°. The residue, a black tar, weighed 1.1 g. The distillate consisted of 1.5 g. of *t*-butyl alcohol and about 1.3 g. of cyclohexenone, which was hydrogenated to cyclohexanone and identified in this form as its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 155°.

Reaction of Potassium *t*-Butylperoxide with Benzyl Halides.—The reaction of the salt and benzyl halides according to the technique described above does not give an isolable intermediate peroxide. Instead, the corresponding aromatic aldehyde is obtained in moderate yield, along with *t*-butyl alcohol. Also obtained are traces of the aromatic acid, though no substituted benzyl alcohol could be isolated. The data for several substituted halides are listed in Table I.

TABLE I

PREPARATION OF ALDEHYDES FROM SUBSTITUTED BENZYL HALIDES

Substd. benzyl halide	Temp., °C.	Time, hr.	Yield of corresponding aldehyde,[a] %	B.p. or m.p., °C., of aldehyde
Benzyl chloride	Reflux	8	23	B. 179
p-Nitrobenzyl chloride	Reflux	3	32	M. 104–5
2-Chloromethyltetralin	Reflux	5	56	B. 126 (10 (mm.)[b]
o-Chlorobenzyl chloride	40	1	74	B. 209
Chloromethylmesitylene	Reflux	5	58	B. 109 (24 mm.)

[a] The aldehydes were characterized as their known 2,4-dinitrophenylhydrazones. [b] 2,4-Dinitrophenylhydrazone, m. p. 199–200°. *Anal.* Calcd. for $C_{17}H_{16}N_4O_4$: C, 59.9; H, 4.69. Found: C, 60.1; H, 4.84.

Acknowledgments.—We wish to thank Glen F. Bailey for infrared analyses, and Geraldine E. Secor for ultimate analyses.

ALBANY, CALIF. RECEIVED SEPTEMBER 12, 1950

[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY[1]]

Kinetics of the Reaction between Potassium *t*-Butylperoxide and Organic Halides

BY GALVIN M. COPPINGER AND TOD W. CAMPBELL

The kinetics of the reaction between three organic halides and potassium *t*-butyl peroxide has been studied at 30 and 50° in methanol solution. The reaction was found to be second-order, with an energy of activation of 21–23 kcal./mole.

In view of the relatively facile production of organic peroxides by a typical displacement reaction[2] it appeared reasonable to suspect that the reaction of the potassium salt of *t*-butyl hydroperoxide and substituted benzyl halides[2a] to give aromatic aldehydes and *t*-butyl alcohol progressed *via* bimolecular mechanism to form an unstable intermediate peroxide. This then decomposed to an aromatic aldehyde and *t*-butyl alcohol

$$ArCH_2Cl + {}^{-}OOC_4H_9\text{-}t \longrightarrow ArCH_2OOC_4H_9\text{-}t + Cl^-$$

$$ArCH_2OOC_4H_9\text{-}t \longrightarrow t\text{-}C_4H_9OH + ArCHO$$

This reaction has been investigated to confirm the order of the first reaction and to determine the velocity constants and the energy of activation for the reaction of *o*-chlorobenzyl chloride[2a] and potassium *t*-butyl peroxide. In addition, the kinetics of the reaction between the peroxide salt and certain other halides were investigated for comparative purposes.

The data collected are summarized in Table I. Since the data indicate that the reaction is clearly second-order, a bimolecular displacement of halogen from the halide is indicated, implying that an intermediate peroxide must exist.

Calculation of the energies of activation for the various reactions (Table I) shows that they are of the same order of magnitude as for the corresponding displacement of halogen by an alkoxide ion (Table II) to give an ether.[3–6]

Experimental

Materials.—Standard solutions of potassium *t*-butyl peroxide (PBP) were prepared by addition of *t*-butyl hydroperoxide (b.p. 46°, 30 mm.) in 15% excess to a standard methyl alcoholic solution of potassium hydroxide. The halides were redistilled commercial products; methanol was reagent grade.

Procedure A.—Freshly prepared solutions of PBP in methanol were allowed to reach the experimental temperature in a thermostated bath and added to a weighed sample of the halide in a volumetric flask. The initial concentration of PBP was checked by titration of a blank at the reaction temperature and corrected for the volume of halide used. The course of the reaction was followed by removing aliquots and titrating the remaining PBP with standard acid, using phenolphthalein indicator. The aliquots were pipetted into 100 ml. of ice-water to which had been added an approximate acid titer, in order to quench the reaction.

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(1) Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

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TABLE I

KINETIC DATA, SOLVENT METHYL ALCOHOL

Halide	Initial concn. of halide, *M*	Initial concn. of peroxide, *M*	Temp., °C.	*K*, l./min.-mole	*E*A, kcal./mole
o-Chlorobenzyl	0.2392	0.0794	29.7	0.00378	
chloride	.1212	.0806	29.7	.00414	
	.0682	.0762	29.7	.00462	
				.00413	
	.1273	.0662	50.2	0.0370	
	.0612	.0668	50.2	.0346	
	.0429	.0669	50.2	.0376	21.5
	.0586	.0674	50.2	.0346	
	.1001	.1102	50.2	.0360	
				.0360	
Allyl bromide	0.1868	0.0921	29.7	0.0606	
	.1005	.0928	29.7	.0576	
	.0452	.0932	29.7	.0594	
				.0582	
	.1314	.0666	50.2	0.489	
	.0717	.0672	50.2	.439	
	.0543	.0670	50.2	.449	20.3
	.0653	.1153	50.2	.451	
	.0670	.0975	50.2	.431	
				.452	
Propyl bromide	0.1663	0.1430	29.7	0.00125	
	.1029	.1049	29.7	.00139	
	.0737	.1051	29.7	.00139	
				.00134	
	.2150	.1053	50.2	0.0141	
	.1164	.1065	50.2	.0139	
	.0736	.1068	50.2	.0147	23.7
				.0142	

TABLE II

KINETIC DATA, SOLVENT ETHYL ALCOHOL

Halide	Reacting anion	Temp., °C.	K, l./min.-mole	*E*A, kcal./mole
Allyl bromide[3,6]	$NaOC_6H_5$	30	0.0676	19.1
Propyl bromide[4]	$NaOC_2H_5$	55	.0328	22[a]
Butyl bromide[5]	$NaOC_6H_5$	25	.000595	
		42.4	.00482	
Benzyl bromide[8]	NaO_6H_5	34.7	.2188	..
Benzyl chloride[6]	$LiOC_6H_5$	34.7	.00358	..

[a] Estimated from authors'[4] data for methyl (20.0), ethyl (21.0) and isobutyl bromide (22.8 kcal.).

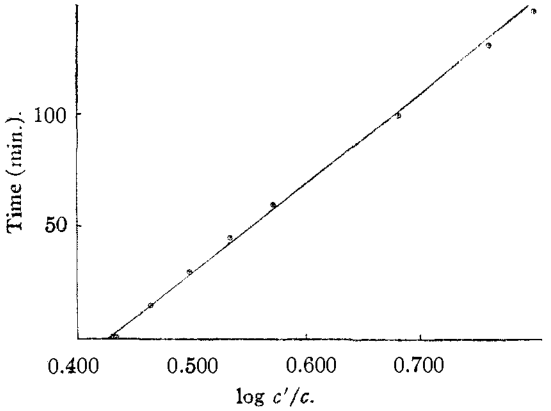

Fig. 1.—Typical experiment. Reaction between potassium *t*-butylperoxide (0.0921 *M*) and allyl bromide (0.1868 *M*) 29.7°: C_I, KO_2-*t*-butyl (0.0921 *M*); C_I', $CH_2{=}CH{-}CH_2Br$ (0.1868 *M*); temp. 29.7°.

Procedure B.—Solutions were prepared as in Procedure A. The course of the reaction was followed by titrating the remaining PBP with nitric acid, using phenolphthalein indicator, then the free halide ion present was measured by titrating with silver nitrate applying fluorescein as indicator. Identical answers were obtained from both methods of titration.[7]

Method of Calculation.—The titration data obtained in this manner were plotted as in Figs. 1 and 2; c and c' are instantaneous concentrations of the reactants at time, t. The value for k was then calculated from the slope of the resulting straight line from the formula; c_I and c_I' are the initial concentrations of the reactants.

$$k = \frac{2.30}{(c_I - c_I')(\text{slope})}$$

Sources of Error.—No correction was made for any competing S_{N1} solvolysis of the halide; estimation of correction factors from available data[6] indicated a maximum error of 4–5% in the values for k. No attempt was made to compare k's obtained at the same ionic strength, although during the course of each experimental run, the ionic strength was constant throughout, if one assumes the activity coefficients of the various ions were essentially one.

As indicated previously,[2a] concentrated methanolic solutions of PBP decompose on refluxing for a short time. The following points regarding the experimental work are presented to show that the data are for the reaction in question alone: (1) The product of decomposition of potassium *t*-butyl peroxide appears to be principally potassium *t*-butoxide, which in the presence of excess *t*-butylhydroperoxide (a relatively strong acid) is instantly reconverted to *t*-butyl alcohol with formation of *t*-butylperoxide ion. (2) Iodometric titrations showed clearly that at the end of each experiment, substantial amounts of peroxide remained, indicating that decomposition of the potassium *t*-butylper-

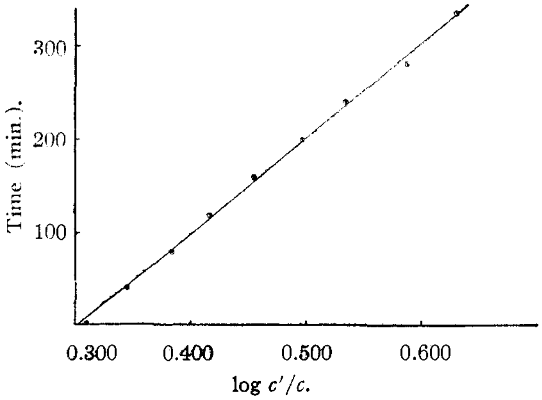

Fig. 2.—Typical experiment reaction between potassium *t*-butylperoxide (0.0622 *M*) and *o*-chlorobenzyl chloride (0.1273 *M*), 50.2°: C_I, KO_2-*t*-butyl (0.0662 *M*); C_I' *o*-chlorobenzyl chloride (0.1273 *M*), temp., 50.2°.

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[7] Our attempts to follow the reaction iodometrically gave less reproducible results than titration of PBP as a base; however, iodometric studies indicated that dilute solutions of PBP were stable under the conditions of the kinetic studies. If initially the hydroperoxide is present at least 15% in excess of the potassium hydroxide, then greater amounts of free hydroperoxide have no measurable effects on the rate up to 50% excess, the limit used in this series of measurements.

oxide was always well under 15%. (3) A standard solution of PBP was left at 50° until all peroxide had disappeared. Excess hydroperoxide was then added, and then a sample of halide. No difference could be detected in the rate of reaction due to the decomposition products. (4) As in (3), except no additional peroxide added. The rate of reaction of the decomposition products with halide is about one-half of the peroxide ion. (5) The excellent linearity of the second-order plots up to nearly complete reaction precludes the possibility that we are studying competing reactions unless they have identical rates.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Direction of Addition to $CFCl=CF_2$ under Free Radical Conditions[1]

BY ALBERT L. HENNE AND DOROTHY W. KRAUS

In the presence of a peroxide, or in ultraviolet irradiation, $CFCl=CF_2$ accepts CF_3I or CCl_3Br to yield $CF_3CFClCF_2I$ or $CCl_3CFClCF_2Br$, respectively. To prove these formulas, $CF_3CFClCF_2I$ was transformed to $CF_3CF=CF_2$ by means of zinc; $CCl_3CFClCF_2Br$ was fluorinated to $C_3F_6Cl_2$ which, by treatment with zinc, also gave $CF_3CF=CF_2$. If addition had taken place in the opposite direction, neither adduct could have given $CF_3CF=CF_2$.

Under free radical conditions, $CF_2=CF_2$ accepts CF_3I to make $CF_3CF_2CF_2I$; the reaction is pictured as promoted by the $CF_3\cdot$ radical, with chain formation of an intermediate $CF_3(CF_2CF_2)\cdot$, and termination by an iodine atom. Promotion by $CF_3\cdot$ rather than $I\cdot$ is, however, merely postulated, not demonstrated.[2]

With an asymmetrically fluorinated olefin, the direction of addition must be experimentally determined, and this additional information may help to establish the reaction mechanism. For this purpose, CF_3I was added to $CFCl=CF_2$, and it was found that the C_3 part of the adduct must be formulated as $CF_3CFClCF_2I$ because its reaction with zinc in alcohol gave nothing but the known[3] $CF_3CF=CF_2$; had the addition occurred in the opposite direction, CF_3CF_2CFClI would have been formed, which could not have been transformed to C_3F_6 by means of zinc.

It is therefore an established fact that the CF_3 group links to the CFCl side of $CFCl=CF_2$. If it is postulated by analogy that the reaction is initiated by a $CF_3\cdot$ radical, an intermediate $CF_3CFClCF_2\cdot$ is formed in preference and possibly to the exclusion of $CF_3CF_2CFCl\cdot$; since it is known from electron diffraction patterns that the bond joining a CF_2 group to another atom is shorter than that involving a CFCl group, an intermediate $CF_3CFClCF_2\cdot$ would represent formation of a weaker C–CFCl bond in preference to a stronger C–CF_2 bond.

For confirmation, the addition of CCl_3Br to $CFCl=CF_2$ was investigated under conditions favoring free-radical reaction. The C_3 fraction was isolated, subjected to conventional fluorination with antimony fluoride and thus transformed into $C_3F_6Cl_2$; the latter, treated with zinc in alcohol under pressure, gave only one product, the known C_3F_6, and must therefore have been $CF_3CFClCF_2Cl$. This in turn means that in the original addition, a CX_3 group became linked to the CFCl side of $CFCl=CF_2$ and parallels the result obtained with CF_3I. Because no compound corresponding to a reversed addition was isolated, it is submitted that the addition may have occurred in one direction only.

A third set of experiments encountered so much side-reacting that it could not be utilized as a confirmation, but it gave qualitative indications which were not at variance with expectations. The addition product from CCl_3Br and $CFCl=CF_2$ was treated with zinc in the hope of forming (and isolating) an olefin $C_3F_3X_3$ and ZnX_2 if its middle group was CClF, or else $C_3F_2X_4$ and ZnFX if the middle group was CF_2. Much decomposition took place, which robbed a fluoride ion test of its significance; the olefin apparently underwent further reaction and the main by-product seemed to be $C_6F_6Cl_2$.

Experimental

Addition of CF_3I.—An equimolecular mixture of CF_3I[4] and $CClF=CF_2$ (0.2 mole each) was placed in the previously described[5] mercury arc equipped container, and maintained under reflux by means of a Dry Ice condenser for a period of 54 hours. The unreacted material, amounting to 3/4 of the batch, was then recovered by low temperature distillation as a mixture boiling around −25°; the remaining 1/4 was left as a liquid residue boiling above room temperature. All of this liquid was treated with zinc in absolute alcohol, and thus transformed into a gaseous material which was caught in a Dry Ice trap; the alcohol solution did not retain more than traces of an organic halide, and a test for fluoride ions proved negative, while a test with silver nitrate gave a voluminous precipitate. The liquefied gas was found to boil at −28°, which is correct for C_3F_6, and it accepted chlorine to yield a compound boiling at 35°, with a refractive index $n^{20}D$ 1.3041, properties which agree with those of the known $CF_3CFClCF_2Cl$.

In another test, an equimolecular mixture of liquefied reagents (0.15 mole each) was sealed in a 1-liter quartz flask, and illuminated with an ultraviolet lamp for 4 weeks. After distilling the unreacted materials, a small amount of liquid (4 to 5 cc.) was collected, treated with zinc in alcohol as above, and the resulting gas chlorinated to yield a liquid (2–3 cc.) b.p. 35°, $n^{20}D$ 1.3047; no other product was seen and a fluoride ion test after the zinc reaction was negative. These results qualitatively parallel those of the preceding test.

In subsequent tests, mixtures of CF_3I and $CF_2=CFCl$ of varied compositions were heated to 85° with small amounts of benzoyl peroxide. Polymerization predominated in all cases, with formation of $CF_3(CF_2Cl)_nI$, from which a monomer could not be isolated.

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