(This generalization also does not depend on the choice of a_{DH}.) Pairing reduces the reactivity of an ion to a disproportionately enhanced degree the greater the pairing energy. This relationship is of obvious potential value. As yet, it is supported by only limited data in a single solvent. Further work is clearly justified.

Table V. Relationship between Free Energy of Dissociation[a] and Differential Free Energy of Activation[b]

Ionophore	$\Delta F_{\mathrm{d}}°$, kcal/mole	$\Delta F_{\mathrm{p}}^* - \Delta F_{\mathrm{f}}^*$,[c] kcal/mole	$(\Delta F_{\mathrm{p}}^* - \Delta F_{\mathrm{f}}^*)/\Delta F_{\mathrm{d}}°$
LiBr	5.75	(2.76)	(0.48)
KCl	5.21	(2.50)	(0.48)
RbCl	5.05	1.94	0.38
KBr	4.80	1.65	0.33
$(CH_3)_4NCl$	3.73	0.99	0.27
$(CH_3)_4NBr$	3.63	1.04	0.29
$(C_2H_5)_4NBr$	3.30	0.49	0.15
$(C_2H_5)_4NCl$	3.24	0.37	0.11

[a] For $a_{\mathrm{DH}} = r_+ + r_-$. [b] Reference state, 1 mole $\mathrm{l.}^{-1}$; $T = 273°$ A. [c] $\Delta F^* = 2.303RT \log (k_{\mathrm{b}}T/k_{\mathrm{r}}h)$, where k_{b}, T, k_{r}, and h are, respectively, Boltzmann's constant, absolute temperature, specific rate, and Planck's constant.

Another potentially important message emerges less clearly[16] from the data of Table V. It is seen that for potassium salts both $\Delta F_{\mathrm{d}}°$ and $\Delta F_{\mathrm{p}}^* - \Delta F_{\mathrm{f}}^*$ are larger for chloride than for bromide. For tetraethylammonium salts the sequence of both quantities is reversed. The behavior of the tetramethylammonium salts appears to be intermediate.[17] A plausible explanation of this behavior lies in the view that chloride ion is more firmly solvated than bromide so that large ions are less able to penetrate its solvation shell than that of bromide. Tetraethylammonium ion is apparently large enough that both the equilibrium and kinetic aspects of pairing are dominated by solvation effects. The equilibrium aspects of this problem are discussed at length elsewhere[10].

The data of Table IV establish that, for the system studied, the nucleophilic reactivity of free bromide is greater than that of free chloride. With $a_{\mathrm{DH}} = r_+ + r_-$ the average value of $k_{\mathrm{f}}^{\mathrm{Br}^-}/k_{\mathrm{f}}^{\mathrm{Cl}^-}$ is 2.52. The difference is relatively small but it is unequivocally in the sequence usually found for nucleophilic attack on sp^3 carbon in protic solvents[18] and opposite to that observed in acetone[19] and in dimethylformamide.[20] It is apparent that the reactivity sequence of unpaired halide ions does not fall into a single general order for aprotic solvents. Interpretation of the sequence observed in liquid SO_2 must await information on the behavior of fluoride and iodide. The reactivity sequence of chloride and bromide is, however, also consistent with dominant influence of solvation of the nucleophilic anions.

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[16] Less clearly because of the fragmentary nature of the kinetic data for KCl.

[17] Precision is low and the relationship depends on choice of a_{DH} for these ionophores.

[18] *Cf., e.g.*, C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

[19] S. Winstein, L. C. Savedoff, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Letters*, [9] 24 (1960).

[20] W. M. Weaver and J. D. Hutchison, *J. Am. Chem. Soc.*, **86**, 261 (1964).

The Induced Decomposition of Acetyl Benzoyl Peroxides[1]

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Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. *Received August 10, 1967*

Abstract: Acetyl benzoyl peroxide decomposes unimolecularly in chlorobenzene at 70°, $k = 2 \times 10^{-5}$ sec^{-1}, but a faster induced process occurs in the pure liquid peroxide. Major products of the induced process (up to 20% each) are *o*- and *p*-toluic acids (absent in the unimolecular reaction), but no *m*-toluic acid. Acetyl 4-chlorobenzoyl peroxide and acetyl 2,6-dichlorobenzoyl peroxide similarly yield 4-chloro-*o*-toluic acid and 2,6-dichloro-*p*-toluic acids, respectively. These results are taken as evidence that the induced reaction involves methyl radical attack on the aromatic ring with concerted cleavage of the peroxide linkage and formation of an α-lactone ring, giving lactones of 1-hydroxy-6- (or -4-) methylcyclohexa-2,4- (or -5-) dienecarboxylic acids, which subsequently rearrange to the toluic acids. Toluene is also a significant product (20%), while the substituted peroxides give *m*-chlorotoluene and 3,5-dichlorotoluene, respectively. It is suggested that these arise from the α-lactones by CO_2 elimination. *The explosive properties of these peroxides are pointed out.*

Experiments reported many years ago by Cass[2] and by Bartlett and Nozaki,[3] together with O^{18} distribution studies by Denney,[4] have shown that the fast induced decomposition of diacyl peroxides in solvents such as ethers involves attack upon peroxide oxygen by α-alkoxyalkyl radicals. In contrast, the slower induced decomposition of benzoyl peroxide in aliphatic hydrocarbon solvents and in carbon tetrachloride (and the induced decomposition at high concentrations in benzene) give significant yields of *ortho*- and *para*-substituted benzoic acids and has led to the proposal by Walling and Savas[5] that here at least one path for the induced chain is radical addition to the aromatic system with concerted cleavage

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[1] Support of this work by grants from the National Science Foundation is gratefully acknowledged.

[2] W. E. Cass, *J. Am. Chem. Soc.*, **69**, 500 (1947).

[3] P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

[4] D. B. Denney and G. Feig, *ibid.*, **81**, 5322 (1959).

[5] C. Walling and E. S. Savas, *ibid.*, **82**, 1738 (1960).

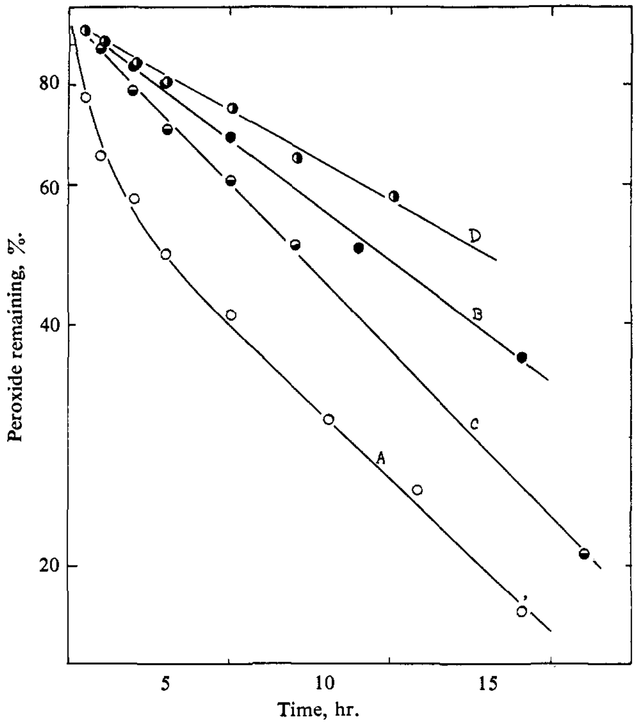
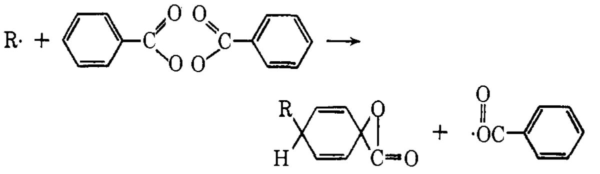


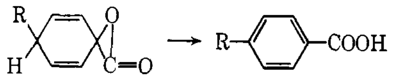
Figure 1. Decomposition of acetyl benzoyl peroxide at 70°: A, neat peroxide; B, 0.2 *M* in chlorobenzene; C, 0.2 *M* in chlorobenzene plus galvinoxyl; D, 0.2 *M* in chlorobenzene plus galvinoxyl by galvinoxyl disappearance.

of the O–O bond and formation of an α-lactone structure, *e.g.*



(1)

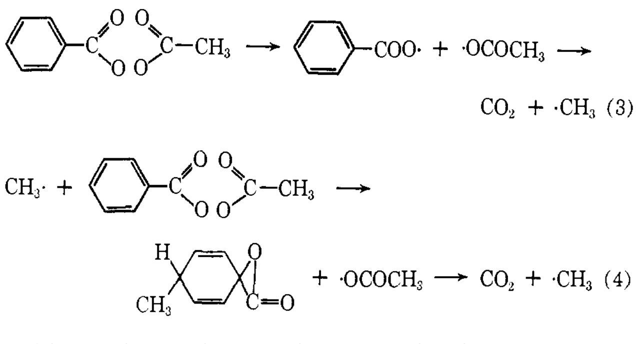
which rearranges to the observed product.



(2)

The principle arguments for the proposed scheme are the exclusive formation of *ortho-* and *para*-substituted products (no comparable concerted process can give rise to *meta* substitution) and the need for some bond-forming process concerted with the addition to provide a driving force to account for the relatively high reactivity of benzoyl peroxide toward radical attack compared with other aromatic systems. (Thus induced decomposition is significant in the presence of a large excess of benzene[6] and the transfer constant of benzoyl peroxide in styrene polymerization at 60° (0.055) is orders of magnitude larger than those for other aromatics.) If lack of comment may be taken as assent, this proposal seems to have been generally accepted, although the problem has had little further direct study.[7,8]

The decomposition of mixed acyl aroyl peroxides such as acetyl benzoyl peroxide should provide an interesting way of studying such induced decompositions, since the peroxide generates its own alkyl radicals without participation of solvent and, taking advantage of the fast decarboxylation of the acetoxy radical, could lead to the chain



(3)
(4)

Although acetyl benzoyl peroxide has been known for many years,[9] decompositions of it and its substituted derivatives have received relatively little study beyond the observation of more or less expected rates and products.[10] This paper reports our results, mostly carried out on molten undiluted peroxides in order to maximize the induced process and restricted in temperature range since the peroxides frequently explode at temperatures above 80°.

Rate Studies. Plots of decomposition of acetyl benzoyl peroxide at 70° under several conditions are shown in Figure 1 and serve to characterize the reaction quite unequivocally. The decomposition rates of 0.2 *M* solutions in chlorobenzene in the absence and presence of galvinoxyl, an efficient radical trap,[11] are in fair agreement, indicating little induced decomposition under these conditions and a rate constant of 2×10^{-5} sec^{-1}.[12] On the other hand, the *slower* apparent rate measured by galvinoxyl disappearance implies that much of the decomposition leads to cage recombination or nonradical products.[13] The rate of decomposition of the neat peroxide is initially considerably faster and the plot is strongly concave upward, indicating significant induced decomposition, the contribution of which decreases as peroxide is consumed.[14] Decomposition of neat peroxide at 75° gave similar results.

Product Studies. The major products of the decomposition of acetyl benzoyl peroxide under several conditions are summarized in Table I.

If we take the products obtained in chlorobenzene as representative of the uninduced decomposition, we see that derivatives of substituted benzoic acids are absent and the low balance for phenyl groups points to

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(6) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946).

(7) F. R. Mayo, R. A. Gregg, and M. S. Matheson, *ibid.*, **73**, 1691 (1951).

(8) The proposal has been criticized by J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, *J. Chem. Soc.*, 3939 (1965). However, they appear to have overlooked the postulated concerted nature of eq 1 in their discussion.

(9) W. R. Jorissen, *Z. Physik. Chem.*, **22**, 34 (1897).

(10) *Cf.*, for example, G. A. Razuvaev and V. N. Latyaeva, *Zh. Obshch. Khim.*, **26**, 1986 (1956).

(11) P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962).

(12) Calculated for the reaction without galvinoxyl. Actually the rate in the presence of galvinoxyl is slightly higher and may indicate some direct reaction with the peroxide at the high concentrations of each (0.2 *M*) employed. In this regard, attempts to use galvinoxyl in neat peroxide led to rapid disappearance of the former.

(13) If the rate of galvinoxyl consumption is compared with the rate of peroxide decomposition without galvinoxyl, efficiency of radical production is approximately 74%. If the galvinoxyl consumption is corrected for the excess rate of peroxide decomposition (assumed to consume galvinoxyl as well), the figure drops to 48%.

(14) The scheme given in eq 3 and 4 predicts a mixed first and three-halves order reaction for the induced process if chains are short.

Table I. Products of Decomposition of Acetyl Benzoyl Peroxide[a]

	Yield, % (based on peroxide decomposed)					
	Temp, °C					
Product	70 (0.2 *M*)	70	70[b]	60	80	60 (uv)
Benzene	2.8	4.1	2.0	3.9	4.3	3.8
Toluene	2.1	9.4	25.1	8.7	10.0	7.9
Methyl benzoate	21.1	20.4	2.8	19.9	22.1	22.7
Biphenyl	...	3.5	5.6	3.5	2.3	1.7
Benzoic acid	23.2	17.8	18.3	17.9	16.4	17.9
o-Toluic acid	...	7.1	17.4	7.0	7.1	7.4
p-Toluic acid	...	5.5	16.7	5.8	5.5	5.3
Methyl *o*-toluate	...	0.3	...	0.4	0.2	0.5
Methyl *p*-toluate	...	0.4	...	0.4	0.2	0.3
Phenyl balance	49.2	68.5	87.9	67.5	71.1	67.5

[a] Neat peroxide unless indicated. [b] Analysis after 10.6% decomposition.

Table II. Decompositions (1 hr) of Acetyl Benzoyl Peroxides

Substituents	Temp., °C	Decompd, %
None	70	34.7
None	75	43.5
4-Chloro	70	23.8
2,6-Dichloro	70	30.5
2,4,6-Trichloro	75	34.2

extensive attack on solvent to yield chlorine-containing polyphenyls which were not investigated further. The high yield of methyl benzoate presumably arises either (or both) from cage recombination of benzoyloxy and methyl radicals or *via* carboxyl inversion. This matter is discussed further when we consider our results with chloro-substituted peroxides. In addition to the products listed, approximately 33% of the methyl groups liberated could be accounted for as a 40:60 mixture of *o*- and *m*-chlorotoluene, showing that chlorobenzene serves as an efficient methyl radical trap in the system and in this way retards the induced decomposition.

Additional products from the neat peroxide compositions presumably reflect contributions from induced decomposition and we may note first that there seems to be little difference between experiments run at 80, 70, and 60° or photochemically at 60°. The most notable change is the appearance of *o*- and *p*-toluic acids (and traces of their esters which could have arisen by ester exchange) although no *m*-toluic acid could be detected. Further, yields are significantly higher in the 70° experiment carried to only 10% decomposition, where, from Figure 1, induced decomposition should be particularly important.

Although these results certainly support our proposed scheme for the induced decomposition, an additional significant product, toluene, remains to be accounted for. Since only traces of toluene were found in the decomposition in chlorobenzene, we conclude that it cannot be a "cage" product and, since the yield is higher in the 10% decomposition, it apparently arises from the induced process, implying an alternative path to eq 4. Further evidence on its nature comes from experiments with acetyl *p*-chlorobenzoyl peroxide, but for the moment we may note that, in the 10% decomposition experiment, toluene and toluic acids account for 60% of the peroxide decomposed. From Figure 1 the initial rate of decomposition of neat peroxide is roughly five times the rate in chlorobenzene, implying that some 80% of the decomposition is induced and 75% of the induced products are thus accounted for. This high figure for the induced decomposition is also supported by the reduced yield of methyl benzoate if it is a "cage" product associated with chain initiation.

Substituted Acetyl Benzoyl Peroxides. Neat decompositions of three chloro-substituted acetyl benzoyl peroxides gave rate curves similar to those in Figure 1, and per cent decompositions in 1 hr, summarized in Table II, indicate slightly lower initial rates. Products of decomposition of the same peroxides appear in Tables III, IV, and V. Unfortunately the experiments were carried out before the importance of limiting reactions to low conversion to emphasize the induced process was appreciated, and accordingly they should be compared with the complete conversion experiments of Table I.

Table III. Decomposition of Acetyl 4-Chlorobenzoyl Peroxide (Neat, 70°)

Product	Yield, %
Chlorobenzene	7.3
m-Chlorotoluene	8.9
Methyl *p*-chlorobenzoate	24.6
p-Chlorobenzoic acid	18.8
p-Chloro-*o*-toluic acid	7.1
p-Chloro-*m*-toluic acid	3.2

Table IV. Decomposition of Acetyl 2,6-Dichlorobenzoyl Peroxide (Neat, 70°)

Product	Yield, %
m-Dichlorobenzene	7.0
3,5-Dichlorotoluene	10.4
Methyl 2,6-dichlorobenzoate	23.6
2,6-Dichlorobenzoic acid	33.1
2,6-Dichloro-*p*-toluic acid	7.5
Methyl 2,6-dichloro-*p*-toluate	1.0

Table V. Decomposition of Acetyl 2,4,6-Trichlorobenzoyl Peroxide (Neat, 70°)

Product	Yield, %
1,3,5-Trichlorobenzene	11.4
2,4,6-Trichlorotoluene	2.0
Methyl 2,4,6-trichlorobenzoate	28.0
2,4,6-Trichlorobenzoic acid	31.2
2,4,6-Trichloro-*m*-toluic acid	7.4
Methyl 2,4,6-trichloro-*m*-toluate	2.2

In every case we see substantial (24–28%) yields of methyl esters to be expected from cage or carboxyl inversion processes.[15] Our data here do not permit us to differentiate unequivocally between the two,[16] but we may note that chlorine substitution, which should facilitate the carboxyl inversion process, produces little increase in yield and that the *photo*decomposition of acetyl benzoyl peroxide itself (Table I), which with

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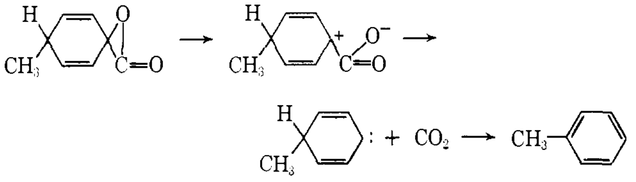
(15) F. D. Greene, H. P. Stein, C. C. Chu, and F. M. Vane, *J. Am. Chem. Soc.*, **86**, 2080 (1964).

(16) The general relation between "polar" and "radical" paths in peroxide decompositions is the subject of another study in this laboratory which we hope to report shortly.

other peroxides favors radical products,[17] shows no decrease in ester yield. All these observations are consistent with a simple cage recombination of benzoyloxy and methyl radicals. On the other hand, Denney and Sherman[18] have reported much higher yields (50–70%) of esters from acyl *m*-chlorobenzoyl peroxides derived from higher aliphatic acids and they believe that here carboxyl inversion is involved.

Turning now to possible products of induced decomposition, Tables III and IV show the chlorotoluic acids expected from *ortho* or *para* attack by methyl radicals in yields comparable to those of the same unsubstituted isomers in Table I. Acetyl 4-chlorobenzoyl peroxide also yields a little (3%) of 4-chloro-*m*-toluic acid which, however, we believe arises from methyl radical attack on peroxide or *p*-chlorobenzoic acid product and not from the induced chain. Particularly significant is the presence of *m*-chlorotoluene in Table III and the 3,5-dichlorotoluene in Table IV, analogous to the toluene in Table I, showing that the point of methyl attack in their formation is *ortho* or *para* to the carboxyl group of the peroxide (*m*-chlorotoluene could not arise alone from methylation of chlorobenzene formed in the reaction since, as noted above, it gives a different product distribution).

Since the same requirement for the driving force of a concerted process arises in the reactions forming toluenes as in those forming toluic acids, there are rigorous limitations on the possible formulations of the reaction. The most likely to us is an alternate decomposition of the postulated α-lactone intermediate, perhaps to a carbenoid species, followed by hydrogen shift, *e.g.*, for the unsubstituted case



A 1,2-shift is easy to contemplate, but the 1,4 shift illustrated would require pronounced puckering of the molecule which , however, seems possible from examination of models.

Finally, we must consider the products from acetyl 2,4,6-trichlorobenzoyl peroxide which, while it might undergo induced decomposition *via* our scheme, cannot yield comparable products by hydrogen shift. Here a small amount of 2,4,6-trichloro-*m*-toluic acid is formed together with its methyl ester. We presume that these arise from nonconcerted methylation of peroxide and of trichlorobenzoic acid and that the considerable amount of ester comes from cage recombination in the subsequent decomposition of the methylated peroxide. In fact, the rate curves for decomposition of this peroxide neat and 0.2 *M* in chlorobenzene are almost identical, suggesting that little induced decomposition actually takes place.

Experimental Section

Peroxides were prepared by autoxidation of the corresponding aldehydes in acetic anhydride solution in the presence of potassium acetate to catalyze the acetylation of the intermediate peracid.[19] Typically 0.1 mole of aldehyde, 0.3 mole of anhydride, and 0.1 g of potassium acetate were stirred together in a flask while dry oxygen was bubbled through the system at 30° under irradiation by an ultraviolet lamp. Yields of 65–80% were obtained after 4 hr. Mixtures were worked up by taking up in ether, stirring for a few hours with water to hydrolyze the anhydride, washing with bicarbonate and water, drying, and removing ether. The peroxides were then purified by recrystallization three times from ligroin and purity was determined by treatment of aliquots with excess sodium iodide in acetic anhydride followed by titration with thiosulfate: acetyl benzoyl peroxide, yield 70%, mp 38°, purity 99.2%; acetyl *p*-chlorobenzoyl peroxide, yield 75%, mp 48°, purity 99.05%; acetyl 2,6-dichlorobenzoyl peroxide, yield 70%, mp 54.5°, purity 99.8% (*Anal.* Calcd for $C_9H_6Cl_2O_4$: C, 43.40; H, 2.42; Cl, 28.47. Found: C, 43.65; H, 2.30; Cl, 28.03); acetyl 2,4,6-trichlorobenzoyl peroxide, yield 78%, mp 71°, purity 99.5% (*Anal.* Calcd for $C_9H_5Cl_3O_4$: C, 38.12; H, 1.77; Cl, 37.52. Found: C, 38.42; H, 2.01; Cl, 38.19).

Decompositions were carried out in sealed degassed tubes using 0.1–1-mmole of peroxide, placed in a thermostat at the desired temperature. *WARNING: neat samples of these peroxides frequently explode when heated above 80°. Explosions sometimes occur at lower temperature and they should be handled with care.*

Rate measurements on neat samples were made by decomposing 0.1-mmole samples as above for varying lengths of time and determining unreacted peroxide by iodometry also as above. Experiments using galvinoxyl were followed (for peroxide) by disappearance of the carbonyl peak at 1795 cm^{-1} and (for gavinoxyl) by the optical density at 435 mμ.

Product Analyses. Reaction mixtures were taken up in ether and acidic components extracted with bicarbonate, converted to methyl esters with diazomethane in ether, and analyzed by gas-liquid partition chromatography (glpc). Nonacidic products were also determined by glpc in both cases using known standards for calibration. In the partial decomposition experiment unreacted peroxide was reduced to acids with sodium iodide solution after extraction of acidic components and these acids were extracted in turn. All products reported (except the small quantity of methyl toluate esters obtained from acetyl benzoyl peroxide where retention time alone was employed) were collected and identified by nmr or infrared spectroscopy usually against known standards. Isomers reported absent were shown to be separated by the glpc column used (SE-30 silicone on firebrick).

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(17) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, 87, 3413 (1965).

(18) D. B. Denney and N. Sherman, *J. Org. Chem.*, 30, 3760 (1965).

(19) C. Walling and E. A. McElhill, *J. Am. Chem. Soc.*, 73, 2927 (1951).