ride. This reaction was not a problem in the kinetic experiments.

2-Chloroanthraquinone was prepared by the cyclization of *o*-(*p*-chlorobenzoyl)-benzoic acid in PPA at 80°. Recrystallization from ethanol gave crystals melting at 209.6–210.2°.

***o*-(*p*-Toluyl)-benzoic acid** was prepared by the Friedel-Crafts reaction of phthalic anhydride and toluene. After purification the crystals melted at 138.7–139.6°. Although high concentrations of *o*-(*p*-toluyl)benzoic acid are known to polymerize in PPA,[20] low concentration, as needed for the kinetic runs, did not result in detectable polymerization during the first four half-lives of the main reaction.

2-Methylanthraquinone.—Matheson, Coleman and Bell practical grade material was recrystallized from ethanol and then sublimed to give crystals melting at 176–177°.

***o*-Phenoxybenzoic Acid and Xanthone.**—The acid had a melting point of 112.8–113.8° after numerous recrystallizations. Xanthone, recrystallized twice from ethanol, had a melting point of 175.6–176.4°.

(20) S. D. Ross and M. Schwartz, *J. Am. Chem. Soc.*, **77**, 3020 (1955).

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE, R. I.]

The Mechanism of Nitrosodecarboxylation of 3,5-Dibromo-4-hydroxybenzoic Acid and Nitrosodeprotonation of 2,6-Dibromophenol

BY KHAIRAT M. IBNE-RASA

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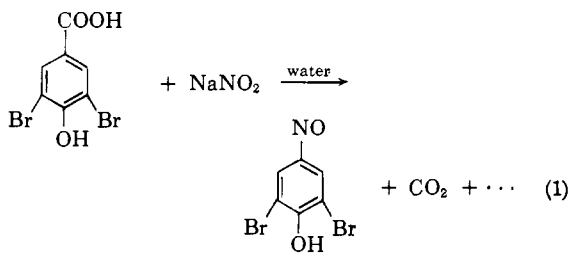
The kinetics of the nitrosodecarboxylation reaction of sodium nitrite with 3,5-dibromo-4-hydroxybenzoic acid has been studied at 30° in aqueous medium. The observed rate law is given in equation 6 of the text. The rates of the nitrosation reaction of sodium nitrite with 2,6-dibromophenol and with 2,6-dibromophenol-4-d_1 have also been measured. A significant kinetic hydrogen-isotope effect (k_H/k_D = 3.6) has been observed. The reaction of the dibromophenol is general base catalyzed while that of the dibromohydroxy acid is not. The observed rate of nitrosodecarboxylation is about 13 times as fast as that of nitrosodeprotonation under identical conditions of acidity and NO_2^- concentration. *p*-Hydroxybenzoic acid reacts at least 300 times more rapidly than does *p*-methoxybenzoic acid. The observed rates of the present reactions are considerably slower than the rate of aniline nitrosation under comparable conditions. These facts are explained on the basis of the reversible formation of a quinonoid intermediate upon the electrophilic attack of the species $H_2O{\cdot}NO^+$ or $NO_2{\cdot}NO$ on the phenolate ion form of the substrate; the subsequent rate-determining loss of CO_2 or H^+ from the quinonoid intermediate leads to the nitrosated product.

Introduction

The reaction of 3,5-dibromo-4-hydroxybenzoic acid with $NaNO_2$ in aqueous or aqueous ethanolic medium (eq. 1) gives 2,6-dibromo-4-nitrosophenol



(1)

with evolution of CO_2.[1] Salicylic acid,[2] *p*-hydroxybenzoic acid and 3-, 4- and 5-methylsalicylic acids also undergo this reaction, but 3-nitrosalicylic acid, 5-nitrosalicylic acid, 3,5-dinitrosalicylic acid and 3,5-dinitro-4-hydroxybenzoic acid do not.[1] The reaction thus appears to be an electrophilic aromatic substitution involving the attack of an NO^+ carrier on the carbon atom bearing the carboxylic group and has been termed nitrosodecarboxylation[1] by analogy with bromodecarboxylation[3] and bromodesulfonation.[4]

The present investigations were undertaken to find out the nature of the nitrosation carrier and to determine whether the over-all mechanism is indeed analogous to that of bromodecarboxylation and bromodesulfonation. A comparison with N-nitrosation of anilines[5–7] on the one hand and with the corresponding brominations[3,4] on the other would be interesting and instructive.

Results

Symbols.—The reactants and the product of the reaction under investigation are acid–base systems. In the following discussion, I will symbolize totally the mixture of the neutral molecule 3,5-dibromo-4-hydroxybenzoic acid and its anionic forms, and II the mixture of 2,6-dibromo-4-nitrosophenol, its tautomer 3,5-dibromo-*p*-quinonemonoxime and their anion; [I], [II] and [NO_2^-] will represent the stoichiometric concentrations, *i.e.*, a total of the concentrations of all the acidic and basic forms of the species enclosed within the brackets.

For a kinetic study of the nitrosodecarboxylation reaction, compound I was chosen as the substrate. Preliminary spectrophotometric studies showed that the reaction of I with aqueous $NaNO_2$ (eq. 1) was uncomplicated by side reactions and that the reaction kinetics could be conveniently measured by following the rate of appearance of the product II in the visible region at 420 mμ, where II has an intense absorption band.[8] The 2,6-dibromo-4-nitrosophenol was prepared according to the method

(1) R. A. Henry, *J. Org. Chem.*, **23**, 648 (1958).

(2) A. A. Nemodruk, *Zhur. Obshchei Khim.*, **26**, 3283 (1956); *C. A.*, **51**, 9528 (1957).

(3) E. Grovenstein, Jr., and U. V. Henderson, Jr., *J. Am. Chem. Soc.*, **78**, 569 (1956).

(4) L. G. Cannell, *ibid.*, **79**, 2927 (1957).

(5) E. D. Hughes, C. K. Ingold and J. H. Ridd, *J. Chem. Soc.*, 58 (1958), and subsequent papers.

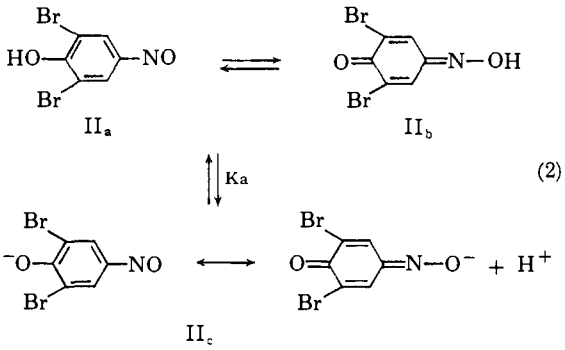
(6) J. O. Edwards, J. R. Abbott, H. E. Ellison and J. Nyberg, *J. Phys. Chem.*, **63**, 359 (1959).

(7) C. A. Bunton and M. Masui, *J. Chem. Soc.*, 304 (1960).

(8) Although the absorption maximum is at 420 mμ, the wave length 425 mμ was monitored for most of the kinetic measurements to avoid any interference by absorption due to nitrous acid at the lower wave length.

described by Henry.[1] Aqueous solutions of II ranging from 4×10^{-6} M to 3×10^{-5} M were prepared and their absorbancies at 425 mμ determined. It was found that Beer's law was not obeyed and that at higher dilutions positive deviations from this law occurred. Since dimerization of the nitroso groups would not be expected to cause this dependence of extinction coefficient (ϵ_{max}) on concentration at such high dilutions,[9,10] it was concluded that the band at 420 mμ is due to the anion of the system II. In the concentration range used, the ionization of the proton must be significant and as dilution is increased the amount of the principal absorbing species, the anion, increases too, giving a higher absorbancy value. Dependence of ϵ_{max} on concentration has been observed in 1,3-diketones and ascribed to the ionization of the enolic form at high dilutions.[11] Solutions of II were, then, buffered and their absorbancies determined in the range 2×10^{-6} M to 4×10^{-5} M at constant pH. Beer's law was found to be operative, with a log $\epsilon_{max} = 4.29 \pm 0.01$ at 425 mμ and at pH 5.06.

The pK_a of II.—The fact that only the anion IIc and not the undissociated tautomers IIa and IIb absorb at 420 mμ was used to determine the pK_a of the system



Ten solutions, each being 2×10^{-5} M in II, were prepared and buffered at pH values ranging from 2.67 to 11.0 at a constant ionic strength of $\mu = 0.8$ and at 30°. Absorbancies of these solutions at 420, 425 and 430 mμ were measured. For each wave length a typical "titration" curve was obtained by plotting absorbancy *versus* pH. The average value of pK_a from the three curves was found to be 4.6 ± 0.1 under the above conditions; K_a is defined by the expression

$$K_a = A_{H^+}[II_c]/[II_a + II_b] \qquad (3)$$

where A_{H^+} is the activity of hydrogen ions and brackets denote concentrations. The value of K_a is, therefore, an apparent ionization constant rather than the true ionization constant of one form. Although in aqueous solutions containing II the predominant species would be expected to be the tautomeric modification IIb,[12-14] K_a cannot be confidently regarded as the ionization constant of IIb without a study of the tautomeric equilibrium. The reliability of the above method was tested by determining the ionization constant K_i, defined by eq. 3a, of p-nitrosophenol (p-quinone monoxime) similarly.

$$K_i = [H^+][\text{anion}]/[\text{neutral forms}] \qquad (3a)$$

$pK_i = 6.2 \pm 0.1$ at 25° and $\mu = 0.2$ (lit.[15] $pK_i = 6.48$ at 25° and $\mu = 0$).

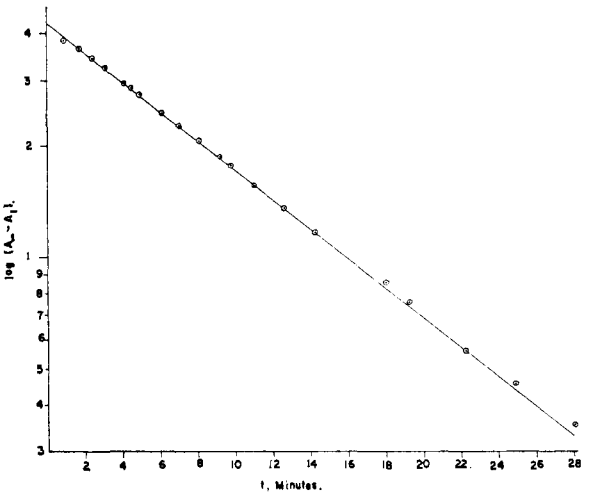


Fig. 1.—Pseudo first-order plot for the nitrosodecarboxylation of 3,5-dibromo-4-hydroxybenzoic acid; $[NO_2^-] = 0.80$ M, pH = 5.02 ± 0.01, $T = 30.0 \pm 0.1°$, $\mu = 0.8$.

Kinetic Method.—In a typical kinetic run an aqueous solution, containing 0.40 M $NaNO_2$, 2×10^{-5} I, 0.40 M $NaNO_3$ and enough perchloric acid to give a desired pH, was prepared at 30°. A sample of this solution was transferred to a spectrophotometric cell thermostated at 30° and the wave length 425 mμ monitored. Inert salt ($NaNO_3$ or $NaClO_4$) was added to maintain a constant ionic strength of $\mu = 0.8$ throughout all measurements. Plots of log $(A_\infty - A_t)$ *versus* time were linear to over 90% reaction (Fig. 1). A_∞ (absorbance at infinite time) was taken as a measure of the total initial concentration of I (preliminary experiments showed that conversion of I to II was quantitative under the kinetic conditions). A_t (absorbancy at time t) was taken as a measure of the concentration of II at time t. Pseudo first-order rate constants were calculated from the slopes of the plots.

Orders.—The linearity of the pseudo first-order plots at a fixed pH and in presence of excess NO_2^- indicates that the reaction is first order with respect to I. This was confirmed by keeping the initial $[NO_2^-]$ and pH constant and varying the initial [I]. The pseudo first-order rate constant was found to be independent of the initial [I] (Table I).

In a set of runs in which pH and initial [I] were constant but the initial $[NO_2^-]$ was varied, the pseudo first-order rate constant was found to vary linearly with the initial $[NO_2^-]$, showing first-order contribution of $[NO_2^-]$ to the rate (Table I).

The order in $[H^+]$ was determined by keeping the initial $[NO_2^-]$ and [I] the same in a set of runs

(9) K. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.*, **78**, 1113 (1956).
(10) K. M. Ibne-Rasa and J. O. Edwards, *ibid.*, **84**, 763 (1962).
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(12) L. C. Anderson and R. L. Yanke, *J. Am. Chem. Soc.*, **45**, 732 (1934).
(13) F. Kehrmann, *Ber.*, **21**, 3315 (1888).
(14) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **27**, 651 (1962).
(15) I. M. Heilbron and H. M. Bunbary, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1938, p. 254.

TABLE I

DEPENDENCE OF PSEUDO FIRST-ORDER RATE CONSTANT (k) ON INITIAL CONCENTRATIONS

No. of runs	$[NO_2^-]$, M	[I], $M \times 10^5$	$[NO_3^-]$, M	$k \times 10^3$, sec.$^{-1}$
2	0.40	2.0	0.40	1.53
1	.60	2.0	.20	2.30
2	.80	2.0	.00	2.95
2	.80	4.0	.00	2.90 ± 0.03

T = 30.0 ± 0.1°, μ = 0.8 and pH = 5.02 ± 0.01

and varying the pH. The pseudo first-order rate constants (k) of these runs were divided by the $[H^+]$ and a pseudo second-order rate constant (k_2) obtained. The results are displayed in Table II. All the runs of Table II were carried out at 30°,

TABLE II

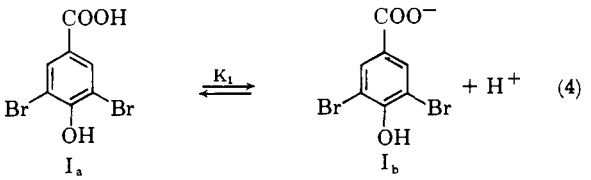
DEPENDENCE OF PSEUDO FIRST-ORDER RATE CONSTANT (k) ON $[H^+]$ AT pH VALUES BELOW 5

No. of runs	pH ± 0.01	$[H^+]$, $M \times 10^6$	$k \times 10^4$ sec.$^{-1}$	$k/[H^+] = k_2$, l. mole^{-1} sec.$^{-1}$
2	4.51	53.7	51.8	96.5
2	4.68	36.3	35.6	98.1
1	4.91	21.4	20.3	94.9
2	5.02	16.6	15.3	92.2

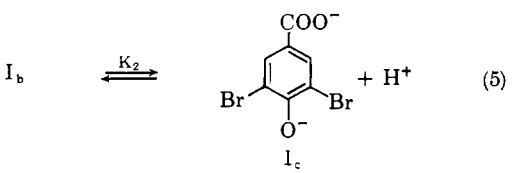
T = 30.0 ± 0.1°, μ = 0.8, $[NO_2^-]$ = 0.40 M, [I] = 2 × 10^{-5} M and $[NO_3^-]$ = 0.40 M. $[H^+]$ was calculated using the expression pH = $-\log [H^+] - \log f\pm$; $-\log f\pm$ was calculated to be 0.24 at μ = 0.8

at a total ionic strength of μ = 0.8 with initial $[NO_2^-]$ = 0.40 M, initial [I] = 2 × $10^{-5}M$ and $[NO_3^-]$ = 0.40 M.

The linear dependence of k on $[H^+]$ or the constancy of k_2 (Table II) shows that the reaction is first order in $[H^+]$ in the region of pH 4.51 to 5.02. In Table III are given the results of a set of experiments carried out at pH values increasing above 5. It can be seen (Table III) that there is an apparent change of order in $[H^+]$ at pH values above 5. In order to find out if this behavior was due to the acid–base equilibria involved in the present system, the dissociation constants for the following equilibria were determined as described below.



(4)



(5)

The values of pK_1 and pK_2 (eq. 4 and 5) at 30° and essentially zero ionic strength were found to be 3.8 ± 0.1 and 6.1 ± 0.1, respectively. At μ = 0.8, pK_2 was found to be 5.6 ± 0.1. In the pH range used for the runs of Table II, therefore, I exists chiefly as Ib (eq. 4), while above pH 5 (Table III) the second ionization into Ic (eq. 5) begins to become significant. Near the pK_2 the kinetic order in $[H^+]$ becomes about 1.5 (Table III). The significance of these facts will be discussed later.

TABLE III

DEPENDENCE OF PSEUDO FIRST-ORDER RATE CONSTANT (k) ON $[H^+]$ AT pH VALUES ABOVE 5

No. of runs	pH ± 0.01	$[H^+]$, $M \times 10^6$	$k \times 10^4$ sec.$^{-1}$	$k/[H^+] = k_2$, l. mole^{-1} sec.$^{-1}$
1	4.72	33.1	63.5	192
2	5.02	16.6	29.2	176
2	5.33	8.13	11.7	144
2	5.64	3.98	3.70	93

T = 30.0 ± 0.1°, $[NO_2^-]$ = 0.80 M, [I] = 2 × 10^{-5} M, μ = 0.8

Ionization Constants of Ia. — The very low solubility of Ia in water does not permit the determination of its ionization constants by titration methods. These constants were, however, conveniently determined spectrophotometrically. Preliminary experiments showed that an aqueous solution of I at pH 1.25, where both the protons must be un-ionized, has an absorption maximum at 257 mμ, while an aqueous solution of the same compound at pH 7 has a new absorption band at 278 mμ. Twenty-four solutions, each containing 4 × 10^{-5} M of I, were prepared (at 30° and μ = 0.0) ranging in pH values from 1.25 to 11.45 and their ultraviolet spectra studied. By superposition of these spectra it was discovered that at 257 mμ the mononegative anion Ib and the doubly negative anion Ic were isosbestic and that at 278 mμ the neutral molecule Ia and Ib were isosbestic. Furthermore Ia did not absorb at 310 mμ, while both Ib and Ic did so. Plots of absorbancies against pH values at wave lengths 257, 278 and 310 mμ gave typical "titration curves" from which pK_1 and pK_2 were found to be 3.8 ± 0.1 and 6.1 ± 0.1, respectively. The value of pK_1 calculated from the Hammett relation is 3.78. Since the above values were determined at essentially zero ionic strength, pK_2 was redetermined at μ = 0.8 in a new set of experiments and found to be 5.6 ± 0.1 at 30°. K_2 is defined by an expression similar to eq. 3.

Absence of Catalysis by Buffer Components. — In a few runs the rates of nitrosodecarboxylation were measured in acetate buffers. Presence of 0.4 M acetate did not have any special catalytic effect on the rates beyond what would be expected of the usual salt effect. When all other conditions were the same the pseudo first-order rate constants were the same within experimental error, whether the reaction mixture contained 0.40 M of NO_3^-, ClO_4^- or AcO^-.

Order in I at Higher [I]. — The order with respect to the substrate I was determined using initial [I] in the range 10^{-3} to 2 × 10^{-3} in 80% water–20% ethanolic medium (20% ethanol by volume was necessary to keep the substrate in solution in this concentration range) by a method similar to that described earlier. Even though the [I] was 100-fold greater than those used to establish the order in [I], the reaction was still first order in I.

Over-all Rate Law. — It has been shown in the preceding section that the rate of nitrosodecarboxylation is first order each in [I] and $[NO_2^-]$.

Also the reaction is first order in $[H^+]$ below *p*H 5, while above this *p*H the order in $[H^+]$ begins to get greater than unity with a tendency to approach 2 as the *p*H increases. In the region of *p*H 4.51 to 5, the concentration of Ia (eq. 4) will be vanishingly small and Ib (eq. 4) the predominant species. Above *p*H 5 ionization of Ib to Ic (eq. 5) begins. The apparent change of order in $[H^+]$ is best explained if the rate law is assumed to be that indicated by eq. 6.

$$\text{rate} = k'[\text{Ic}][NO_2^-][H^+]^2 \quad (6)$$

When the order in $[H^+]$ is clearly one, one of the two protons is furnished by the ionization of Ib to Ic in an equilibrium prior to the rate step. At higher *p*H values this proton is only partly available from the ionization of Ib, until at *p*H 5.64 ($pK_2 = 5.6 \pm 0.1$) the order in $[H^+]$ becomes $\simeq$1.5. The rate law thus implies that in the transition state the doubly negative anion Ic, an NO_2^- and two protons are involved. The validity of this rate law (eq. 6) was tested by treating the data of Tables II and III as follows.

In the *p*H range studied (4.51 to 5.64) the relationships expressed by eq. 7 and 8 hold and from these eq. 9 is derived.

$$K_2' = [H^+][\text{Ic}]/[\text{Ib}] \quad (7)$$

$$[\text{Ib}] + [\text{Ic}] = [\text{I}] \quad (8)$$

$$[\text{I}] = \frac{K_2'[\text{I}]}{[H^+] + K_2'} \quad (9)$$

Substituting the value of [Ic] in eq. 6 we get eq. 10.

$$\text{rate} = k'K_2'[\text{I}][NO_2^-]\left\{\frac{[H^+]^2}{[H^+] + K_2'}\right\} \quad (10)$$

At constant *p*H and in presence of excess of NO_2^-, the observed pseudo first-order rate constant (k) is defined by eq. 11.

$$\text{rate} = k[\text{I}] \quad (11)$$

$$\text{Thus } k' = \frac{k\{[H^+] + K_2'\}}{K_2'[H^+]^2[NO_2^-]} \quad (12)$$

K_2' is calculable from K_2. In Table IV are listed values of k', calculated by using eq. 12 and the pseudo first-order rate constants (k) of Tables II and III. The constancy of k' over the entire range of *p*H studied shows that the rate law of eq. 6 is indeed valid.

TABLE IV

EVALUATION OF NITROSODECARBOXYLATION RATE CONSTANT

*p*H ± 0.01	$[H^+] \times 10^5$, *M*	$[NO_2^-]$, *M*	$k \times 10^4$ sec.$^{-1}$	$k' \times 10^{-5}$, l.^{2} mole^{-2} sec.$^{-1}$[a]
4.51	53.7	0.40	51.8	651
4.68	36.3	.40	35.6	683
4.72	33.1	.80	63.5	676
4.91	21.4	.40	20.3	703
5.02	16.6	.40	15.3	716
5.02	16.6	.80	29.2	691
5.33	8.31	.80	11.7	674
5.64	3.98	.80	3.70	587

[a] k' is defined by eq. 6; $\mu = 0.8$, $T = 30.0 \pm 0.1°$.

Comparison of Rates between the Reactions of *p*-Hydroxybenzoic Acid and *p*-Anisic Acid. — In a single kinetic run a 50% aqueous ethanolic solution containing 0.01 *M* *p*-hydroxybenzoic acid and 0.20 *M* $NaNO_2$ was prepared at 30° and the appearance of *p*-nitrosophenol followed by monitoring the wave length 410 mμ. Using the extinction coefficient of an authentic sample of *p*-nitrosophenol under the kinetic conditions, an estimated value of the initial rate of reaction from a concentration–time plot was found to be 3.7×10^{-3} % sec.$^{-1}$. The *p*H meter reading of the reaction mixture was 6.65.

In another experiment a 50% aqueous ethanolic solution containing 0.01 *M* *p*-anisic acid and 0.20 *M* $NaNO_2$ was kept at 30°. The wave length 730 mμ, where *p*-nitrosoanisole has an estimated ϵ_{max} of about 45, was monitored. There was no observable formation of *p*-nitrosoanisole over a period of 48 hr. The possibility that nitrosodecarboxylation might have occurred and the product escaped detection because of rapid subsequent reactions like oxidation was eliminated by pipetting out aliquots of the reaction mixture at widely spaced time intervals and diluting them 200-fold with water. Ultraviolet spectra of these diluted samples were studied. The shape and height at λ_{max} (248 mμ) of these spectra were identical within ±2% of each other (last aliquot taken 48 hr. after mixing of reactants) and with that of a solution of just *p*-anisic acid of comparable strength. It was thus demonstrated that not more than 2% of *p*-anisic acid could have reacted at the end of 48 hr., which corresponds to a maximum rate of reaction of 1.2×10^{-5}% sec.$^{-1}$. The *p*H meter reading was 6.48. The observed minimum value of the ratio $k_{p\text{-OH}}/k_{p\text{-OCH}_3}$ is thus 300.

The Kinetics of Nitrosation of 2,6-Dibromophenol. — The reaction of 2,6-dibromophenol (III) with nitrous acid (hereafter nitrosodeprotonation) to form II is analogous to nitrosodecarboxylation in that the net outcome of both reactions is the substitution of NO^+ in the ring in a position *para* to the activating phenolic group. They differ only in the nature of the displaced species, H^+ being displaced from III and CO_2 from I. The kinetics of nitrosodeprotonation was measured by the method described for nitrosodecarboxylation. The results are given in Table V.

TABLE V

PSEUDO FIRST-ORDER RATE CONSTANT (k_1) FOR NITROSODEPROTONATION OF III AT 30.0 ± 0.1° AND μ = 0.8

No.	*p*H ± 0.01	$[NO_2^-]$, *M*	[III], $M \times 10^5$	Added salt, *M*	$10^4 k_1$, sec.$^{-1}$
1	4.72	0.80	2.0	..	4.88
2	4.72	.80	4.0	..	4.93
3	4.72	.40	4.0	0.40[a]	2.02
4	4.72	.40	4.0	.40[b]	2.09
5	4.72	.40	1.0	.40[c]	3.41
6	4.65	.40	4.0	.40[c]	3.80
7	5.02	.80	2.0	..	2.33

[a] NO_3^-, [b] ClO_4^-, [c] AcO^-.

The data of Table V show: (1) The reaction is first order with respect to III (runs 1 and 2) and first order in $[H^+]$ in the *p*H range studied (runs 1 and 7). (2) The order in $[NO_2^-]$ is not exactly one. Doubling the initial $[NO_2^-]$ from 0.40 *M* to 0.80 *M* increases the rate by about 20% over and above a factor of two (runs 1, 2, 3 and 4). (3) Addition of

0.40 M acetate, in place of 0.40 M NO_3^- or 0.40 M ClO_4^-, causes an increase of about 70% in the rate (runs 3, 4, 5). (4) NO_3^- and ClO_4^- do not appear to have any special effect on rate beyond the usual salt effect. (5) 2,6-Dibromophenol (III) undergoes nitrosation with an observed pseudo first-order rate constant (Table V) which is smaller than the observed pseudo first-order rate constant for nitrosodecarboxylation of I (Table III) by a factor of 13, the pH and $[NO_2^-]$ being same in the two cases.

Catalysis by Buffer Components.—It is interesting to note (Table V) that nitrosodeprotonation is catalyzed by acetate ion. Also the discrepancy from the first-order dependence on $[NO_2^-]$ in this reaction is easily explained if it is assumed that the excess rate over the first-order contribution of $[NO_2^-]$ is due to catalysis by NO_2^-. Nitrosodeprotonation thus appears to be general base catalyzed in contrast with nitrosodecarboxylation which is neither acetate catalyzed nor NO_2^- catalyzed.

The Dissociation Constant of III.—For a proper comparison between the rates of nitrosodeprotonation and nitrosodecarboxylation, the pK_a (defined by an expression similar to eq. 3) of III was determined spectrophotometrically in a manner similar to that described for the ionization constants of I and II and was found to be equal to 6.4 ± 0.1 at 30° and μ = 0.8.

Search for Intermediates.—Attempts were made in the study of both reactions to obtain spectral evidence for the possible quinonoid intermediates; the method was similar to that used by Cannell[14] in studies of the bromodesulfonation reaction. A 50% water–50% ethanolic solution containing 0.01 M I and 0.20 M NO_2^- was prepared at 30°. A 1-ml. aliquot of this solution (taken at any time during the first 15–20 min. after mixing) was diluted 100-fold with water. The ultraviolet spectrum of the diluted sample was the same as expected of a 0.0001 M solution of I. Similar results were obtained when III was used as the substrate. Thus a quinonoid intermediate, if any, is not formed in detectable amounts either in nitrosodecarboxylation or in nitrosodeprotonation.

Order in III at Higher Concentrations of III.—The rate studies reported in Table V were carried out with initial [III] in the range 2×10^{-5} M to 4×10^{-5} M. In a new set of experiments, carried out in 75% water–25% ethanolic medium, the order with respect to III was found to be clearly one even when the initial [III] was increased by a factor of 1000 as compared with the initial [III] used for the experiments of Table V.

Kinetic Hydrogen-isotope Effect.—2,6-Dibromophenol-4-d_1 (IV) was prepared by deuterium exchange upon 2,6-dibromophenol according to an early method[16,17] as modified by Grovenstein and Aprahamian.[18] The rate of the reaction of the ring-deuterated dibromophenol IV with aqueous sodium nitrite (nitrosodedeuteration) was measured under the conditions: $[NO_2^-]$ = 0.80 M, [IV] = 4×10^{-5} M, pH = 4.74 ± 0.01, T = 30.0 ± 0.10° and μ = 0.8. The pseudo first-order rate constant (k_D) under these conditions was found to be 1.23 ± 0.02 $\times 10^{-4}$ sec.$^{-1}$. This value of k_D is an average of three kinetic runs. Under identical conditions the pseudo first-order rate constant (k_H) for the unlabeled dibromophenol III is 4.45×10^{-4} sec.$^{-1}$. The hydrogen-isotope effect (k_H/k_D) is thus 3.6.

(16) C. K. Ingold, C. G. Raisen and C. L. Wilson, *J. Chem. Soc.*, 1637 (1936).

(17) A. P. Best and C. L. Wilson, *ibid.*, 28 (1938).

(18) E. Grovenstein, Jr., and N. S. Aprahamian, *J. Am. Chem. Soc.*, **84**, 212 (1962).

Discussion

Summary of Results.—The results of the present investigations which are pertinent to the reaction mechanism are itemized as: (1) The observed rate law for nitrosodecarboxylation is

$$\text{rate} = k' \left[\text{Br}_2\text{C}_6\text{H}_2(\text{COO}^-)(\text{O}^-) \right] \left[NO_2^- \right] \left[H^+ \right]^2 \qquad (6)$$

(2) p-Hydroxybenzoic acid reacts at least 300 times as fast as p-methoxybenzoic acid. (3) Nitrosodeprotonation is catalyzed by acetate ion while nitrosodecarboxylation is not. Furthermore, whereas the latter reaction is clearly first order in NO_2^-, the former is greater than first order in the same species. (4) Nitrosodeprotonation is substantially faster than nitrosodedeuteration (k_H/k_D = 3.6). (5) There is no change in kinetic order with respect to the substrate III even when the initial [III] is increased 1000-fold as compared with the concentrations at which the rate law was established. Similarly there is no change in order with respect to I (nitrosodecarboxylation) even after a 100-fold increase in the initial [I]. (6) The observed pseudo first-order rate constant for nitrosodecarboxylation is ~13 times as large as that for nitrosodeprotonation at comparable pH and $[NO_2^-]$. (7) In neither of the two reactions studied is there formed an intermediate in quantities large enough to be detectable spectroscopically. (8) The rate of aniline nitrosation (which is the rate of formation of $NO_2 \cdot NO$) at 0°, pH = 5.02, $[NO_2^-]$ = 0.01 M and μ = 0.1 is known to be 4×10^{-8} mole l.$^{-1}$ sec.$^{-1}$.[5] The rate of the nitrosodecarboxylation reaction extrapolated to these conditions from the present data is about 2×10^{-10} mole l.$^{-1}$ sec.$^{-1}$ when initial [I] = 4×10^{-5} M and μ = 0.8. Thus the formation of $NO_2 \cdot NO$ is about 200 times as fast as the observed rate of nitrosodecarboxylation under conditions which are comparable except in total ionic strength.

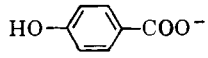
The kinetic data suggest that in both of the reactions studied the transition state is composed of the substrate and a nitrosation carrier. Since the present substrates can exist in various acidic and basic forms, and since the effective nitrosation carrier can be one (or more) of a number of possible carriers, elucidation of these aspects will be attempted along with that of the mechanism of substitutions.

The dependence of rate on $[H^+]$, first order below pH 5 and greater than first order as pH is increased beyond 5, has been interpreted as being due to the involvement of Ic (the dinegative ion of the dibromohydroxyacid) in the transition state. This view is further supported by a comparison of the observed rates of nitrosodecarboxylation of p-

hydroxybenzoic acid and *p*-methoxybenzoic acid ($k_{OH}/k_{OCH_3} \simeq 300$). An estimate of this ratio can be had, for the assumed case where the mononegative ion of *p*-hydroxybenzoic acid is the species nitrosated, from the relationship given in eq. 13. For aromatic electrophilic substitutions the value

$$\log k_{OH}/k_{OCH_3} = \rho(\sigma_{OH}^{+} - \sigma_{OCH_3}^{+}) \qquad (13)$$

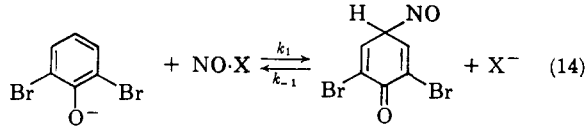
of ρ, the reaction constant, varies between -4 and -10 and $\sigma^{+}_{p\text{-}OH}$ and $\sigma^{+}_{p\text{-}OCH_3}$ the substituent constants, are -0.92 and -0.778, respectively.[19] Even using a relatively high value of ρ (-10), the ratio k_{OH}/k_{OCH_3} is calculated to be $\simeq 14$. Thus the predicted value of 14, which should be a maximal value, is far less than the experimentally observed value of ~ 300. This eliminates the anion A, as well



A

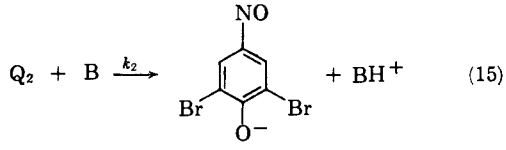
as the neutral molecule, as the species involved in nitrosodecarboxylation. The conclusion is clear that the doubly negative anion of the hydroxyacid is the species being nitrosated and is in keeping with the observed rate law and with the types of compounds which undergo nitrosative decarboxylation.

Nitrosodeprotonation.—The existence of a significant kinetic hydrogen-isotope effect (k_H/k_D = 3.6) and of general base catalysis in nitrosodeprotonation[20] is interpreted in terms of a two-step mechanism involving the reversible formation of a quinonoid intermediate, Q_2, which then undergoes loss of the proton to give the nitrosated product (eq. 14, 15).



(14)

Q_2

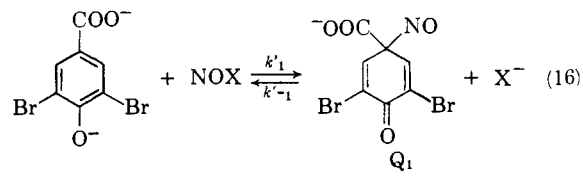


(15)

where B is the solvent or an added base and NO·X is the nitrosation carrier. Since the reaction is general base catalyzed and since the kinetic hydrogen-isotope effect is pronounced, the step involving the cleavage of the C–H bond (eq. 15) must be rate determining. The failure to see the quinonoid intermediate spectroscopically presumably stems from the fact that $k_{-1} >> k_2$. The reversal step thus does not permit the accumulation of Q_2 into detectable concentrations.

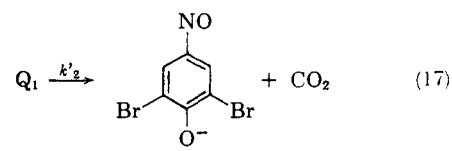
The present data are not inconsistent with a single transition state mechanism, in which the base pulls away the proton synchronously with the attack of the electrophile on the carbon carrying the proton. Such a termolecular mechanism, however, is considered to be unlikely as being operative in aromatic electrophilic substitutions.[18,21–23] It has never been definitely established and it does not explain the much greater ease with which aromatic electrophilic substitutions occur in contrast with their aliphatic analogs.[22] On the contrary, there is convincing evidence for a quinonoid intermediate mechanism in some cases.[3,4] The view that the two-step mechanism offers a superior interpretation of the present data is in accord with the views of other authors. Thus the iodination of aniline where general base catalysis has been demonstrated to be kinetically important,[24] the iodination of phenol where the ring deuterated phenol reacts at only one-fourth the rate of the unlabeled phenol[25] and aromatic sulfonation where H^3 is substituted considerably more slowly than H^1,[26] are all believed to follow the two-step mechanism with the second step being rate controlling.

Nitrosodecarboxylation.—In view of the arguments advanced in the foregoing section a two-step rather than a concerted (SE2) mechanism is favored for nitrosodecarboxylation also (eq. 16, 17).



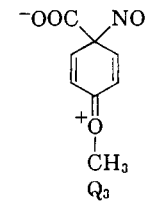
(16)

Q_1

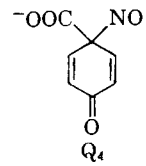


(17)

Although the data in this case cannot discriminate whether the formation of the intermediate ($k_2' >> k'_{-1}$) or its decomposition ($k'_{-1} >> k_2'$) is rate-limiting, it is considered that the latter condition obtains by analogy with nitrosodeprotonation. The great difference between the reactivities of *p*-hydroxybenzoic acid and *p*-methoxybenzoic acid arises from the fact that in the latter case the expected intermediate Q_3 has a higher energy content than that of the intermediate Q_4 arising from the dinegative ion of the *p*-hydroxyacid.



Q_3



Q_4

(19) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(20) Here the reasonable assumption is made that acetate catalysis in nitrosodeprotonation is not due to the introduction of an additional carrier but is rather attributable to the fact that the base aids in the departure of the leaving proton. Nitrite ion is similarly assumed to act as a general base toward the leaving proton. The assumption is justified by the absence of acetate or nitrite catalysis in nitrosodecarboxylation and by the presence of a large kinetic hydrogen-isotope effect in nitrosodeprotonation.

(21) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 279.

(22) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp. 417–418.

(23) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 334.

(24) Reference 22, p. 445.

(25) E. Grovenstein, Jr., and D. C. Kilby, *J. Am. Chem. Soc.*, **79**, 2972 (1957).

(26) L. Melander, *Arkiv Kemi*, **2**, 213 (1950).

Either the energy of activation for the formation of Q_3 is too high for it to form under our conditions, or, if it is formed, the ratio k_{-1}/k_2 is so large that none of it can go to products. The data at hand do not distinguish as to which one of these two is the controlling feature.

There are other mechanisms conceivable for nitrosodecarboxylation but they cannot be reconciled with the present data. 3,5-Dibromo-4-hydroxybenzoic acid undergoesnitrosation at an apparent rate which is 13 times as fast as the rate of the nitrosation of 2,6-dibromophenol (item 6, in the summary of results). Furthermore, the latter reaction is general base catalyzed while the former is not. These data eliminate the possibility that nitrosodecarboxylation proceeds through a rapid protodecarboxylation followed by the rate-determining nitrosation of the resulting 2,6-dibromophenol. Also eliminated is the possibility of a rate-controlling protodecarboxylation followed by a rapid nitrosation step, because the reaction is first-order with respect to the nitrosation carrier. The formation of the intermediate ArCOO·NO followed by rearrangement and decarboxylation, although kinetically allowed, will not be considered because simpler mechanistic paths are available and because the influence of substituents would not be expected to be as large as observed. ArCOOBr has been rejected as an intermediate in bromodecarboxylation on similar grounds.[3]

Nitrosation Carrier.—The term nitrosation carrier has the same significance here as in the nitrosation of anilines.[5] It may be free NO^+ or NO^+ combined with an anionic base such as NO_2^- or with a neutral base such as H_2O. In the simplest system, such as the present one where buffers were made by adding appropriate amounts of perchloric acid to aqueous sodium nitrite solutions, the possible carriers in order of decreasing electrophilic reactivity[5] are: NO^+, $H_2O{\cdot}NO^+$, $NO_2{\cdot}NO$, HO·NO. Nitrosonium perchlorate is not included in this list because it does not exist in molecular form.[5] During the present investigations kinetic runs were carried out at times with 0.40 M $NaNO_3$ and at others with 0.40 M $NaClO_4$ to maintain a total ionic strength of $\mu = 0.8$. There was observed no special effect on rate when NO_3^- replaced ClO_4^-.

It has been argued that the most attractive explanation of the data on nitrosodeprotonation, and by implication of that on nitrosodecarboxylation, is the two-step mechanism with the second step being rate determining. On the basis of this mechanism none of the above four possible carriers is incompatible with the observed kinetics. However, NO^+ and HO·NO may reasonably be eliminated as effective agents on the following grounds.

Ingold and his co-workers[5] found that in weakly acidic aqueous media NO^+ and HO·NO are ineffective as carriers of nitrosation in the diazotization of anilines; the former species is not formed in these conditions and the latter, because of its inherent weakness as an electrophile, is useless as a direct nitrosating agent. It thus appears unlikely that in the present reactions, where conditions of acidity similar to those of aniline nitrosation were employed, NO^+ or HO·NO would be the operative carrier. The number of the probable carriers is thus narrowed down to two, $H_2O{\cdot}NO^+$ or $NO_2{\cdot}NO$.

In the assumed case that $NO_2{\cdot}NO$ is the effective carrier, the mechanism would be that represented by eq. 18–23.

$$NO_2^- + H^+ \rightleftharpoons HNO_2 \quad \text{fast} \quad (18)$$

$$HNO_2 + H^+ \rightleftharpoons H_2O{\cdot}NO^+ \quad \text{fast} \quad (19)$$

$$H_2O{\cdot}NO^+ + NO_2^- \rightleftharpoons NO_2{\cdot}NO + H_2O \quad \text{fast} \quad (20)$$

$$Ib \rightleftharpoons Ic + H^+ \quad \text{fast} \quad (21)$$

$$Ic + NO_2{\cdot}NO \rightleftharpoons Q_1 + NO_2^- \quad \text{fast} \quad (22)$$

$$Q_1 \longrightarrow \text{products} \quad \text{slow} \quad (23)$$

It should be possible in principle to increase the initial [I] to a limit that the nucleophilic attack of NO_2^- upon $H_2O{\cdot}NO^+$ (eq. 20) rather than the decomposition of Q_1 (eq. 23) is made rate controlling. In such a situation the order of reaction with respect to I will fall from one to zero and the rate will have an upper limit, which will be equal to the rate of nitrosation of aniline. On the other hand, when $H_2O{\cdot}NO^+$ is assumed to be the effective species, it will not be possible to bring about a change in the kinetic law by similar means and there will be no upper limit to the rate because, then, only fast equilibria occur before the rate step.

The rate of formation of $NO_2{\cdot}NO$ as measured by aniline nitrosation is about 200 times as fast as the observed rate of nitrosodecarboxylation (item 8, summary of results) when the initial [I] = $4 \times 10^{-5} M$. Thus, in order to test whether $NO_2{\cdot}NO$ is the nitrosating agent or not, it would be necessary to increase the observed rate of nitrosodecarboxylation by a factor of more than 200 by increasing the initial [I] from 4×10^{-5} M to over 10^{-2} M. When attempts were made to achieve this end, it was found that the initial [I] could not be increased to beyond 2 to 4×10^{-3} M, because of solubility problems. Although at these higher concentrations the order of reaction with respect to I was still clearly one, the results are inconclusive.

At the present stage, then, it is difficult to decide whether the effective carrier of nitrosonium ion in the present system is $H_2O{\cdot}NO^+$ or $NO_2{\cdot}NO$.

Acknowledgment.—This work was done in the laboratory of Professor John O. Edwards, to whom the author is indebted for his kind interest and for counsel. Acknowledgment is also due to Rev. R. M. Ewing, Principal Forman Christian College, Lahore, West Pakistan, for grant of leave and to Miss Nan Sorensen for technical assistance with some of the experiments.

Experimental

Materials.—3,5-Dibromo-4-hydroxybenzoic acid was prepared according to the method described by Grovenstein and Henderson,[3] and 2,6-dibromo-4-nitrosophenol was prepared by the method of Henry.[1] 2,6-Dibromophenol, Eastman Kodak Co., white label, was further purified by recrystallization from ethanol–water mixtures. 2,6-Dibromophenol-4-d_1 was prepared by deuterium exchange upon 2,6-dibromophenol; the method of Grovenstein and Aprahamian[18] was followed closely, except that a small amount of p-dioxane was added to the reaction mixture to make the system homogeneous. The deuterated product after two sublimations melted at 56.5–57°. It did not depress the m.p. of a pure sample of the unlabeled dibromophenol. The infrared spectrum (KBr pellet) of the deuterated product was different from that of the unlabeled com-

pound in certain respects. Thus, for example, 2,6-dibromophenol had two bands (in μ) at 13.2(strong) and 13.0-(medium), both assignable to C–H out-of-plane deformations.[27] These two bands were absent from the spectrum of the deuterated product and their complete absence was taken to indicate that the deuterium exchange had essentially gone to completion. The best grades available of other materials were used.

Kinetic Method.—In a typical kinetic run 40 ml. of an aqueous solution containing $NaNO_2$, $NaNO_3$ and the dibromohydroxy acid was brought to 30.0 ± 0.1° and then 10 ml. of aqueous perchloric acid of appropriate strength, which had also been previously brought to the same temperature, was added. The time of addition of perchloric acid was taken as zero time. About 3 ml. of this reaction solution, which contained 4×10^{-5} M dibromohydroxy-acid, 0.40 M $NaNO_2$ and 0.40 M $NaNO_3$, was transferred to a thermostated spectrophotometric cell immediately after mixing. The cells were maintained at 30.0 ± 0.1°. The wave length 425 mμ was monitored for the appearance of 2,6-dibromo-4-nitrosophenol. It was confirmed that Beer's law was obeyed in buffered solutions and that no other materials present in the reaction solution absorbed at 425 mμ. The pH was measured at the end of the reaction; Beckman pH meter model GS was used for most of the measurements. It was found in preliminary experiments that the absorbancy at infinite time (A_∞) of a reaction solution containing $4 \times 10^{-5}M$ dibromohydroxy acid was the same as that of a $4 \times 10^{-5}M$ solution of 2,6-dibromo-4-nitrosophenol at identical pH, showing that the conversion of the acid to the nitroso compound was quantitative. When 2,6-dibromophenol or its 4-deuterated form was the substrate, the conversion to the nitroso compound was about 90%. Therefore, for nitrosodeprotonation, A_∞ used was that from a parallel run on the dibromohydroxy acid under identical conditions. The rate constants reported for nitrosodeprotonation are, therefore, obtained from a study of the first 40–50% of the reaction.

The equilibrium constants of the various related systems were determined by methods described in the section entitled Results.

(27) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 65.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, N. J.]

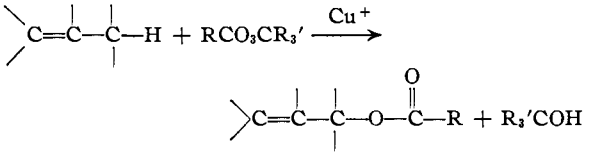
A Study of the Copper Ion Catalyzed Reactions of t-Alkyl Peresters with Several Olefins

BY DOROTHY Z. DENNEY, ARTHUR APPELBAUM AND DONALD B. DENNEY

RECEIVED JUNE 29, 1962

Optically active Δ^1-p-menthene was allowed to react with t-butyl peracetate in the presence of copper ion to give a mixture of menthenyl acetates. Saponification and chromic acid oxidation afforded a mixture of ketones from which the optically inactive semicarbazone and 2,4-dinitrophenylhydrazone of 2-methyl-5-isopropylcyclohex-2-eneone were obtained. Tetramethylethylene reacted with t-butyl perbenzoate in the presence of copper ion to give 2,3-dimethylbut-1-ene-3-yl benzoate. Trimethylethylene yielded a mixture of benzoates. The major components, *ca.* 87%, was shown to be 2-methylbut-1-ene-3-yl benzoate.

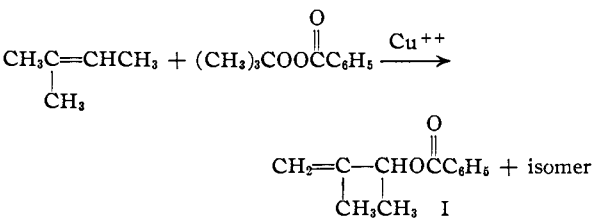
Kochi[1] has very lucidly summarized existing knowledge on the copper salt catalyzed reactions of peroxides. Of particular interest is the reaction of t-alkyl peresters with olefins in the presence of copper ions. This is a typical allylic substitution process which leads to introduction of an ester function



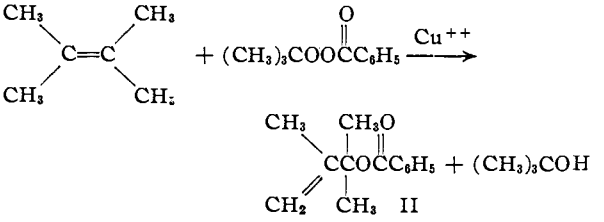
α to the double bond. Considerable confusion has arisen because of the reports that this substitution occurs without double bond isomerization.[2,3] Recently Kochi[4] has shown that *cis*-2-butene, *trans*-2-butene and 1-butene react with t-alkyl peresters in in the presence of copper ions to give the same mixture of butenyl benzoates.[5] Although there is no question about the intervention of an intermediate which allows equilibration over the allylic positions in the butene reactions, a general demonstration that this is the case in olefins more highly substituted about the double bond has not been provided. It was the purpose of this work to investigate such systems.

Results and Discussion

Trimethylethylene was allowed to react with t-butyl perbenzoate in the presence of cupric ion. A two-component mixture of methylbutenyl benzoates was obtained in 70% yield. The major



component of the mixture was separated by careful fractionation. Hydrogenation afforded 2-methyl-3-benzoyloxybutane. Thus the major product of the reaction was 2-methyl-3-benzoyloxy-1-butene (I). Similarly, tetramethylene gave a 78% yield of 2,3-dimethyl-3-benzoyloxy-1-butene (II) contaminated with 3% methyl benzoate.



(1) J. K. Kochi, *Tetrahedron*, **18**, 483 (1961).

(2) (a) M. S. Kharasch and G. Sosnovsky, *J. Am. Chem. Soc.*, **80**, 756 (1958); (b) M. S. Kharasch, G. Sosnovsky and N. C. Yang, *ibid.*, **81**, 5819 (1959).

(3) D. B. Denney, D. Z. Denney and G. Feig, *Tetrahedron Letters*, **No. 15**, 19 (1959).

(4) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 774 (1962).

(5) Substantially the same results have been obtained in this Laboratory by D. Z. D.