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Effect of Solvent Acidity on the Rate of Nitric Acid Oxidation of Cumene*[1]

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It is known that the nitric acid oxidation of cumenes gives acetophenones,[1] but the reaction scheme is unknown. Cumene is oxidized in our hands with 3.0M nitric acid for 6 hr at 90°C in 60% dioxane to give acetophenone as a major product in a yield of 70—76% together with benzoic acid (*ca.* 30%). The products were identified by means of UV and GLC. In view of these products, the intermediate may be dimethylphenylcarbinol, since, in our previous study, it has been observed that the nitric acid oxidation of triphenylmethane gives triphenylcarbinol quantitatively under the similar conditions to the present reaction.[2] The formation of acetophenone is considered to be the result of the oxidative demethylation of an intermediary dimethylphenylcarbinol. If *t*-alkoxy radical is formed, ketone is generally obtained.[3] In fact, under the present conditions, dimethylphenylcarbinol gave acetophenone in a yield of 71% together with benzoic acid after 6 hr. Also acetophenone was oxidized to benzoic acid with nitric acid under the present conditions.

Thus the pathway for the nitric acid oxidation of cumene is considered as follows:

$$PhCH(CH_3)_2 \rightarrow PhC(CH_3)_2OH \rightarrow PhCOCH_3 \rightarrow PhCOOH$$

Here, hydrogen atom abstraction from cumene is of interest in connection with the oxidation of triphenylmethane.[2] In excess nitric acid, the rate of consumption of cumene should be in agreement with that of hydrogen abstraction from cumene. The reaction mixture was extracted with chloroform at appropriate time intervals as described before,[2] and the rate was followed by measuring the consumption of cumene by means of GLC with a column of 1 m packed with Apiezon grease L 15% on Celite 545 at 100—160°C, using chlorobenzene as an internal standard.

In the nitric acid oxidation of diphenylmethane, triphenylmethane[2] and benzoin,[4] the rate was explained in terms of the ionization potential and bond-dissociation energy of the C–H bond which is cleaved, where the attacking species were considered to be both HNO_2^+ and NO_2. Since cumene is more reactive than toluene, the methyl group of cumene facilitates the oxidation in the present reaction. In order to disclose the attacking species in the oxidation of cumene, it is intended to measure the effect of acidity of solution on hydrogen abstraction.[2,4]

The first-order rate constants measured in excess nitric acid are shown in Table 1. As obvious in Table 1, the rate is first-order in cumene. The rate is independent of the amount of sodium nitrite added, but when a considerable amount of urea (a scavenger of nitrous acid) was added, a fairly long induction period was observed (Table 1).

Nitrous acid is an initiator but it does not affect the oxidation rate, *i. e.*, the concentration of NO_2 is constant at the stationary state as reported before;[4-6] hence, the rate is expressed as follows: $v=k[\text{cumene}]$.

The acidity effect on the rate is shown in Fig. 1.

TABLE 1. EFFECT OF INITIAL CONCENTRATIONS OF REACTANTS IN NITRIC ACID OXIDATION OF CUMENE IN 60% DIOXANE AT 90°C[a)]

$[PhCH(CH_3)_2]$, M	$[NaNO_2]$, M	Induction period, min	$10^4 k$, sec^{-1}
0.058	0.01	10—20	2.1
0.034	0.01	10—20	2.1
0.059	0	~20	2.0
0.058	0.005	10—20	2.0
0.056	0.015	10—20	2.0
0.059	0.2[b)]	>150	—

a) Initial concentration, $[HNO_3]$=3.0M.
b) $CO(NH_2)_2$ was added instead of sodium nitrite.

[*1] Contribution No. 152.

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[3] D. G. Alder, M. W. T. Pratt and P. Gray, *Chem. Ind.* (London), **1955**, 1517; A. D. Yoffe, *ibid.*, **1954**, 963; A. A. Zavitsas and S. Seltzer, *J. Amer. Chem. Soc.*, **86**, 3836 (1964).

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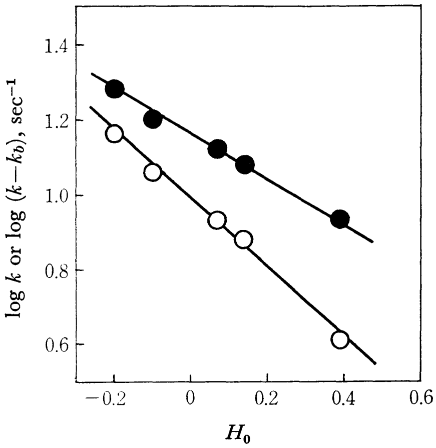


Fig. 1. Acidity effect of the solution on the rate for nitric acid oxidation of cumene in 60% dioxane at 90°C.

Initial concentration: $[\mathrm{HNO_3}]=2.0\,\mathrm{M}$, $[\mathrm{NaNO_2}]=0.01\,\mathrm{M}$, $[\mathrm{PhCH(CH_3)_2}]=0.059\,\mathrm{M}$, $[\mathrm{H_2SO_4}]=0-1.0\,\mathrm{M}$. ●, Plot of log k *vs.* H_0; ○, Plot of log $(k-k_b)$ *vs.* H_0.

The plot of log k *vs.* H_0 gave a line with a slope of a fractional number (−0.5), which is analogous to that for triphenylmethane, *etc.* (Fig. 1). Hence, k may be expressed as follows: $k=k_ah_0+k_b$. The plot of $10^5\,k$ *vs.* h_0 gives the value of k_b to be 4.5×10^{-5}. The plot of $\log(k-k_b)$ *vs.* H_0 gave a straight line with a slope of *ca.* −1 as expected.

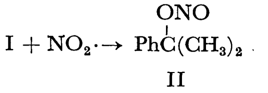
These facts suggest a mechanism involving simultaneous attack of both $\mathrm{HNO_2^+}$ and $\mathrm{NO_2}$ as in the case of diphenylmethane and triphenylmethane.

$$\mathrm{HNO_3 + HNO_2 \rightleftarrows 2NO_2 + H_2O} \qquad (1)$$

$$\mathrm{H^+ + NO_2\cdot \rightleftarrows HNO_2^{\dot{+}}} \qquad (2)$$

$$\mathrm{PhCH(CH_3)_2 + HNO_2^{\dot{+}} \xrightarrow{slow} \underset{I}{Ph\dot{C}(CH_3)_2} + H_2NO_2^+} \qquad (3)$$

$$\mathrm{PhCH(CH_3)_2 + NO_2\cdot \xrightarrow{slow} I + HNO_2} \qquad (4)$$

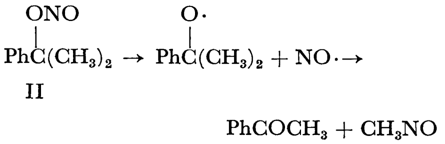


$$\mathrm{I + NO_2\cdot \rightarrow \underset{II}{Ph\overset{ONO}{\overset{|}{C}}(CH_3)_2}} \qquad (5)$$

$$\mathrm{II + H_2O \rightarrow PhC(CH_3)_2OH + HNO_2} \qquad (6)$$

$$\mathrm{PhC(CH_3)_2OH \xrightarrow{HNO_3} PhCOCH_3 \xrightarrow{HNO_3} PhCOOH}$$

It is known that alkyl nitrite is easily hydrolyzed even at 0°C.[7] Therefore, II may be rapidly hydrolyzed to dimethylphenylcarbinol, but the direct formation of acetophenone may not be excluded.



$$\mathrm{\underset{II}{Ph\overset{ONO}{\overset{|}{C}}(CH_3)_2} \rightarrow Ph\overset{O\cdot}{\overset{|}{C}}(CH_3)_2 + NO\cdot \rightarrow PhCOCH_3 + CH_3NO}$$

This mechanism leads to the rate equation:

$$v = (k_3[\mathrm{HNO_2^{\dot{+}}}]+k_4[\mathrm{NO_2\cdot}])[\mathrm{cumene}]$$
$$= (k_3K_2[\mathrm{H^+}]+k_4)[\mathrm{NO_2\cdot}][\mathrm{cumene}]$$

Here, k and K are rate and equilibrium constants of subscripted steps, respectively.

The methyl group of cumene may facilitate the oxidation due to both lowering the ionization potential of C–H bond[8] and the stability of intermediate radical (I). Hence, two kinds of attacking species, $\mathrm{NO_2}$ and $\mathrm{HNO_2^{\dot{+}}}$, should participate in the oxidation as observed in the case of di- and triphenylmethanes,[2] and benzoin.[4]

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