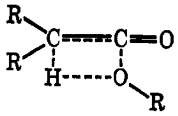
alcohols the reaction proceeds through a cyclic transition state B, but one involving only one molecule of 3-pentanol.



B

Our kinetic results are compatible with all of the reports in the literature which show that diarylketenes are more reactive than dialkylketenes in the acylation of alcohols. This is probably due to some degree of charge separation in the transition state and the ability of the aryl group to stabilize the activated complex by smearing out any carbanionic character at the α-carbon atom.

The smaller second-order rate constant for dibromoketene as compared to dichloroketene is exactly as expected. A consideration of both electronic and steric factors would suggest this result. The chlorine atoms are more capable of stabilizing any carbanionic character in the transition state due to the greater inductive ability and steric crowding will be more predominant with dibromoketene due to the larger bromine atoms.

The difference in rate of the three dialkylketenes would appear to be solely due to steric effects. An examination of molecular models reveals that the butyl group in butylethylketene is certainly large enough to present a steric problem for the bulky 3-pentanol molecule. Consequently, it would appear that steric considerations are the controlling factor in dialkylketene reactivities.

In conclusion, our solvent effect data suggest that the acylation of alcohols with ketenes proceeds by a one-step process which probably involves a cyclic transition state. Also, the halogen atoms in the dihaloketenes studied apparently do not markedly influence the rereactivity of the ketene in the acylation of alcohols; *e.g.*, these ketenes exhibit about the same reactivity as dialkylketenes but both are less reactive than diphenylketene.

Experimental Section

Dichloroketene was prepared by the dehalogenation of trichloroacetyl bromide and isolated in hexane as previously described by us.[6] Dibromoketene was prepared by the dehalogenation of tribromoacetyl bromide and also isolated in hexane as one of us has previously reported.[7] Diphenylketene was prepared by the dehydrochlorination of diphenylacetyl chloride with triethylamine.[11] Diethylketene was obtained by the pyrolysis of diethylmalonic anhydride according to the procedure of Duckworth.[12] We are grateful to Eastman Chemical Products, Inc., for supplying us with butylethylketene in the form of a 20% solution in toluene. The toluene was removed under reduced pressure and the ketene distilled and dissolved in dry hexane for kinetic runs. Dimethylketene was prepared by the pyrolysis of the ketene dimer, tetramethyl-1,3-cyclobutanedione.[13]

Apparatus.—A constant-temperature water bath was employed with an immersion heating element coupled to a Fisher proportional temperature controller that afforded a temperature control of ±0.02°. The rate of disappearance of 3-pentanol was followed by vpc. An Aerograph AP-40 operating with a thermal conductivity detector was used with a 10 ft × 0.25 in. column packed with 15% Ucon and 2% Oronite on 30/60 mesh white Chromosorb. An oven temperature of 95° was employed. *n*-Octane was used as an internal standard. Least-squares rate constants were calculated on an IBM 1620 computer. Only a slight excess of 3-pentanol was employed in all runs and the concentrations ran about 0.05 *M*.

3-Pentyl Alkanoates.—A hexane solution of the ketene was treated with an excess of 3-pentanol. The hexane and excess alcohol were removed by distillation. The esters were distilled under reduced pressure through a 6 in. Vigreux column, ir absorption (smear) 1730–1770 cm^{-1}. The more detailed data are recorded in Table I.

Acknowledgments.—The authors are grateful to The Robert A. Welch Foundation and the National Science Foundation (GP-7386) for their generous support of this work.

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Kinetics of the Nitric Acid Oxidation of Diphenylmethane to Benzophenone[1]

YOSHIRO OGATA, HIROSHI TEZUKA, AND TADASHI KAMEI

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

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The mechanism of nitric acid oxidation of diphenylmethane to benzophenone has been kinetically studied with *ca.* 2.5 *M* HNO_3 in 70 vol. % aqueous acetic acid at 90°. The reaction shows an induction period, sodium nitrite being an effective initiator. At the nitrous acid concentration over 0.02 *M*, where the solution is probably saturated with NO_2, the rate is expressed as $v = k[C_6H_5CH_2C_6H_5]$, *i.e.*, the rates are independent of concentrations of nitric and nitrous acids. The k value increases with increasing acidity of the media, the plot of log k *vs.* H_0 giving a straight line with a slope of *ca.* -1. A possible mechanism is proposed which involves a rate-determining abstraction of α-hydrogen atom from diphenylmethane by protonated NO_2.

The kinetic studies on the nitric acid oxidation of some substrates, *e.g.*, benzyl alcohol,[2] benzyl ether,[3] and benzaldehyde,[4] have been reported from this laboratory, where aqueous dioxane has been used as a solvent. Dioxane is a suitable solvent, but it may be decomposed by nitric acid, while acetic acid is a stable solvent for oxidation. It is known that diphenylmethane is oxidized to benzophenone by dilute nitric acid,[5] but its mechanism has not yet been reported.

(1) Contribution No 116.

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The oxidation of diphenylmethane by 2.5 *M* nitric acid in 70 vol. % acetic acid–30 vol. % water as a solvent at 90° gave benzophenone (the yield of isolated product was 84%, but the yield estimated by ultraviolet spectrophotometry was *ca.* 100%). The present paper describes kinetic study on the oxidation mechanism of diphenylmethane to benzophenone in aqueous acetic acid followed by ultraviolet spectrophotometry.

Results and Discussion

Induction Period.—The oxidation of diphenylmethane with pure nitric acid at 90° shows an induction period; *e.g.*, the induction period of 85 min is observed with 2.5 *M* nitric acid at 90° (Table I). Sodium nitrite and hydroquinone are effective initiators for the reaction, but azobisisobutyronitrile and benzoyl peroxide, which are known to be effective initiators for the radical reaction, do not initiate the reaction. The concentration of nitrous acid on addition of hydroquinone was followed, where it was observed that a considerable amount of nitrous acid was formed from the start of reaction; *e.g.*, 0.016 *M* nitrous acid was detected at 20 min after addition of 0.0103 *M* hydroquinone to a mixture of nitric acid and 70% acetic acid at 90°. In contrast, no nitrous acid was observed on addition of benzoyl peroxide or azobisisobutyronitrile. Hence, HNO_2-producing materials can be initiators.

Table I

Effect of Added Compounds on the Nitric Acid Oxidation of Diphenylmethane at 90°

Added compd	Concn,[f] *M*	Induction period, min
None	...	85[d]
None	...	30[e]
$NaNO_2$	0.010	17[d]
$NaNO_2$	0.010	7[e]
$NaNO_2$	0.015	12[d]
$NaNO_2$	0.020	7[d]
AIBN[a]	0.00502	>240[d]
AIBN[a]	0.0103	>210[d]
AIBN[a]	0.0104	17[e]
BPO[b]	0.00526	136[d]
BPO[b]	0.00992	120[d]
BPO[b]	0.0111	20[e]
H_2Q[c]	0.0101	9[d]

[a] Azobisisobutyronitrile. [b] Benzoyl peroxide. [c] Hydroquinone. [d] 70 vol. % acetic acid. [e] 60 vol. % dioxane. [f] Initial concentration: $[HNO_3] = 2.50\ M$, $[Ph_2CH_2] = 0.050\ M$.

Effect of Nitrous Acid and Solvent on the Rate.—The effect of nitrous acid was studied for the nitric acid oxidation of diphenylmethane with excess nitric acid. Figure 1 shows plots of log $[a/(a - x)]$ *vs.* time. The plots are affected by the concentration of nitrous acid at low concentration of added nitrous acid; *i.e.*, the rate constant increases initially with proceeding of the reaction, *i.e.*, with increasing nitrous acid concentration in the system (Table II), but, after *ca.* 30% conversion, the rate constant approaches to a definite value. On addition of a high amount of sodium nitrite the rate constant held constant from the start of reaction. This phenomenon seems to show that nitrogen dioxide (NO_2) is saturated in the solvent aqueous acetic acid at high concentration of nitrous acid, but that NO_2 is not saturated at the lower nitrous acid concentration, thus giving an irregular rate constant until the saturation is attained.

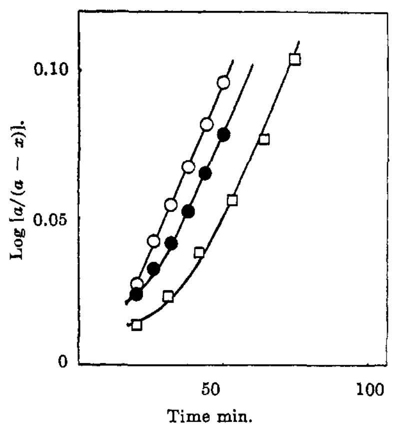


Figure 1.—First-order plot for the nitric acid oxidation of diphenylmethane in 70 vol. % acetic acid at 90°. Initial concentration: $[HNO_3] = 2.50\ M$, $[Ph_2CH_2] = 0.050\ M$; ○, $[NaNO_2] = 0.02\ M$; ●, $[NaNO_2] = 0.01\ M$; □, $[NaNO_2] = 0.005\ M$.

Table II

Nitrous Acid Concentration in the Reaction Mixture in 70 Vol. % Acetic Acid at 90°[a]

Time, min	$[HNO_2]$, *M*	Time, min	$[HNO_2]$, *M*
40	0.0138	160	0.0365
80	0.0207	200	0.0260
120	0.0314	240	0.0268

[a] Initial concentration: $[HNO_3] = 2.50\ M$, $[NaNO_2] = 0.01\ M$, $[Ph_2CH_2] = 0.0516\ M$.

The saturation of NO_2 is easily attained in the solvent aqueous dioxane, and hence the effect of increasing concentration of nitrous acid is not observed. This independence of rate on $[HNO_2]$ has been reported in the nitric acid oxidation of benzyl ether,[3] and benzaldehyde[4] in aqueous dioxane.

The induction period is shorter in dioxane than in acetic acid and an appreciable amount of nitrous acid was formed in a dioxane solution of pure aqueous nitric acid without addition of diphenylmethane after 40 min. The dioxane would be decomposed a little by nitric acid, giving NO_2 which initiates the reactions. Hence, the concentration of NO_2 or attacking species formed by the reaction of nitric acid with nitrous acid may reach the stationary state more readily in aqueous dioxane than in aqueous acetic acid.

The rate in aqueous acetic acid was measured under the conditions where the rate constant held constant; *i.e.*, the solution may be saturated with NO_2.

Rate Equation.—The oxidation using excess nitric acid fits to the rate equation $v = k_1$(diphenylmethane), and is shown in Table III. The effect of various initial concentrations of nitric acid on k_1 was studied in the presence of 1.5 *M* sulfuric acid which should maintain the acidity. The corrected k_1 values to the same acidity function of the solution ($H_0 = -1.20$) were independent of the initial concentration of nitric acid as shown in Table III.

Effect of Acidity.—The reaction was accelerated by increasing the acidity of the solution. The acidity plot of log k_1 *vs.* H_0 gave a straight line with a slope of *ca.* −1 (Figure 2).

Effect of Temperature.—The first-order rate constants (10^5k, sec^{-1}) were 3.85 at 80°, 5.70 at 85°, 8.34

TABLE III

FIRST-ORDER RATE CONSTANTS FOR THE NITRIC ACID OXIDATION OF DIPHENYLMETHANE AT VARIOUS INITIAL CONCENTRATIONS OF REACTANTS IN 70 VOL. % ACETIC ACID AT 90°

$[HNO_3]$, M	$[Ph_2CH_2]$, M	10^5k_1, sec^{-1}
2.50	0.0500	13.6
2.50	0.0999	13.9
2.50	0.150	14.0
0.20	0.0501	3.15[a]
0.50	0.0501	3.85[a]
0.70	0.0501	3.83[a]
1.00	0.0501	3.81[a]

[a] These values were obtained in the presence of 1.50 M sulfuric acid and they were corrected to those at $H_0 = -1.20$.

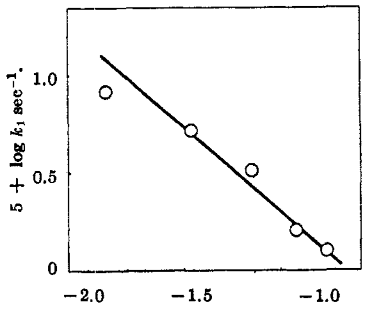


Figure 2.—Plot of log k_1 *vs.* H_0 for the nitric acid oxidation of diphenylmethane in 70 vol. % acetic acid at 90°. Initial concentration: $[HNO_3] = 1.0\ M$; $[NaNO_2] = 0.005\ M$; $[Ph_2CH_2] = 0.0501\ M$; $[H_2SO_4] = 0$–$1.5\ M$.

at 90°, and 15.2 at 95°. The Arrhenius plot afforded a good straight line, which gave the value of 26.5 kcal/mol and −4.8 *eu* for the apparent Arrhenius energy and entropy of activation, respectively.

Mechanism.—The observed facts are summarized as follows: (i) the rate is affected with nitrous acid concentration at lower concentration of nitrous acid, but is independent at higher concentration; (ii) after *ca.* 30% conversion the rate is expressed as $v = k(C_6H_5CH_2C_6H_5)$, and it is independent of nitric acid and nitrous acid concentrations; (iii) the rate is proportional to h_0; (iv) nitrous acid is an effective initiator, but it has no influence on the rate expression in the steady state. These results suggest the mechanism given by eq 1–8. The α-hydrogen abstraction from diphenylmethane (eq 3) is followed by the formation of diphenylmethyl nitrite (eq 4). Hydrolysis of the nitrite gives benzhydrol (eq 5) which is rapidly oxidized to benzophenone. In fact, it was observed that nitric acid oxidation of benzhydrol was too fast to measure under these conditions. If the hydrogen atom abstraction from diphenylmethane (step 3) is rate determining, the rate may be expressed as

$$HNO_3 + HNO_2 \overset{K_1}{\rightleftarrows} 2NO_2\cdot + H_2O \qquad (1)$$

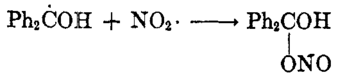
$$NO_2\cdot + H^+ \overset{K_2}{\rightleftarrows} HNO_2\cdot^+ \qquad (2)$$

$$Ph_2CH_2 + HNO_2\cdot^+ \xrightarrow{k_3} Ph_2\dot{C}H + H_2NO_2^+ \qquad (3)$$

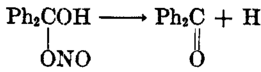
$$Ph_2\dot{C}H + NO_2\cdot \longrightarrow Ph_2CHONO \qquad (4)$$

$$Ph_2CHONO + H_2O \rightleftarrows Ph_2CHOH + HNO_2 \qquad (5)$$

$$Ph_2CHOH + HNO_2\cdot^+ \longrightarrow Ph_2\dot{C}OH + H_2NO_2^+ \qquad (6)$$



$$Ph_2\dot{C}OH + NO_2\cdot \longrightarrow \underset{\displaystyle ONO}{Ph_2COH} \qquad (7)$$



$$\underset{\displaystyle ONO}{Ph_2COH} \longrightarrow \underset{\displaystyle O}{\overset{}{Ph_2C}} + HNO_2 \qquad (8)$$

$$v = k_3[C_6H_5CH_2C_6H_5][HNO_2\cdot^+] = k_3K_2[C_6H_5CH_2C_6H_5][H^+][NO_2\cdot]$$

Protonated nitrogen dioxide has been proposed as a principal attacking species to account for the effect of acidity.[3,4] Protonated nitrogen dioxide is more powerful than NO_2 because of its positive charge and the high acidity of reaction media may permit its existence. If the attacking species were NO_2, the proportionality of the rate with h_0 could not be explained. If the concentration of added nitrous acid is higher than *ca.* 0.01 M in aqueous acetic acid, a considerable amount of nitrogen dioxide should be formed, the evolution of nitrogen dioxide from the system being observed. The solution then reaches the saturation point, *i.e.*, a stationary concentration of NO_2. At low concentration of nitrous acid, however, the observed rate constant, $k_3K_2[NO_2]$, should continue to increase until the concentration of nitrogen dioxide becomes constant. This is in accord with observation.

The ionization potential of $Ph_2\dot{C}H$ is comparatively small (7.32 eV),[6] hence its conversion into Ph_2CH^+ (eq 3) may be expected to be fairly rapid; *i.e.*, the hydride ion abstraction may be possible, although there is no decisive evidence.

Naturally, some electrophilic species from nitric acid, *e.g.*, nitronium ion (NO_2^+), may be present in the present reaction mixture. However, these cations are less probable as attacking species because of the existence of long induction period. Moreover, nitrous acid or nitrosonium or nitrite ion cannot be attacking species, since the rate is independent of either nitric or nitrous acid concentration.

Experimental Section

Materials.—Diphenylmethane was prepared by the Friedel–Crafts reaction of benzene with benzyl chloride,[7] bp 119–121° (10 mm) [lit.[8] bp 121–122° (9 mm)]. Benzhydrol was prepared by the reduction of benzophenone with zinc dust, mp 66–67° (lit.[9] mp 68°).

A Typical Procedure for Kinetic Experiments.—A mixture of diphenylmethane and nitric acid in 70 vol. % acetic acid was thermostated at 90°. The reaction was started by the addition of aqueous 0.005–0.02 M sodium nitrite. A given amount of the reaction solution was pipeted out, and the product was extracted with chloroform. The extract was diluted to *ca.* $2.0 \times 10^{-5}\ M$ with methanol, and the concentration of benzophenone was measured by means of ultraviolet spectrophotometry. The absorption of benzophenone in methanol was as follows: λ_{max} 252 mμ (log ϵ 4.38). Nitrous acid was measured spectrophotometrically at 535 mμ after treatments with sulfanilic acid and then α-naphthylamine.

Measurement of the Acidity Function.—The Hammett acidity function was measured spectrophotometically according to the method of our previous papers[2–4] using 4-chloro-2-nitroaniline as an indicator.

Registry No.—Diphenylmethane, 101-81-5; benzophenone, 119-61-9; nitric acid, 7697-37-2.

Acknowledgment.—The authors are grateful to Mr. T. Nakamura for his assistance.

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