Relative Rates of Chromic Acid Oxidation of Naphthalenes and Fluorenes in Acetic Acid

YOSHIRO OGATA AND HIROYUKI AKIMOTO

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In the chromic acid oxidation of diphenylmethane[1] and toluenes[2] in acetic acid, the rates were found to be first-order with respect to the substrate and second-order with respect to chromium trioxide, the rates being retarded by the presence of chromic acetate. The present paper is an extension of these studies and deals with kinetics of the chromic acid oxidation of naphthalene, 1-nitronaphthalene, fluorene and 2-nitrofluorene in acetic acid. The rates were measured by the estimation of remaining chromium trioxide by iodometry.

The rates of the oxidation of anthracene and 1-acetylanthracene were too fast to measure.

The rate constants were calculated graphically using the same equation as for toluenes:

$$dx/dt = k[a - (x_c/g)][b - x]^2[b - x - (y/h)] \quad (1)$$

where a is the initial concentration of substrate (moles/l.), b that of chromium trioxide, x the decreased concentration of chromium trioxide after t seconds, x_c the corrected x in which the oxidation of the solvent is considered, y the concentration of chromic acetate, and g and h are empirical constants. Typical runs are shown in Fig. 1 and the rate constants thus calculated are listed in Tables I and II. Here, the values of g and h are both equal to 2. The data on carbon dioxide estimation, evolved by the oxidation of fluorenes, are summarized in Table II.

TABLE I

FOURTH-ORDER RATE CONSTANTS CALCULATED BY EQ. 1 FOR TYPICAL RUNS IN FIG. 1

Time (min.)	$k \times 10^3$ (mole/l.)$^{-3}$ sec.$^{-1}$
Naphthalene, 0.0313*M*; CrO_3, 0.0119*M*; Temp. 30°	
5	0.820
15	0.868
23	0.973
31	0.976
	Av. 0.898
α-Nitronaphthalene, 0.0477*M*; CrO_3, 0.0116M; Temp. 40°	
12	0.0780
30	0.0850
50	0.0927
70	0.0843
	Av. 0.0853

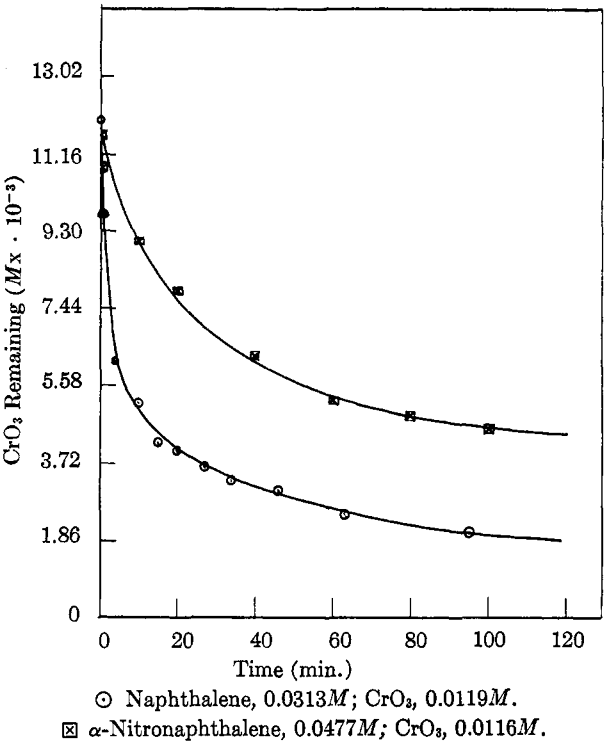

Fig. 1. Typical runs for the chromic acid oxidation of naphthalene at 30° and α-nitronaphthalene at 40°

TABLE II

RATES OF THE OXIDATION IN ACETIC ACID

Compound	Mole[a]/L.	Mole[b]/L.	Temp.	$k \times 10^3$ (mole/l.)$^{-3}$ sec.$^{-1}$	ΔH‡ Kcal./Mole
Naphthalene	0.0237	0.0119	30 ± 0.1	1.11	
	0.0313	0.0119	30 ± 0.1	0.898	
	0.0530	0.0108	30 ± 0.1	0.758	
1-Nitronaphthalene	0.0258	0.0109	40 ± 0.1	0.0799	
	0.0596	0.0108	40 ± 0.1	0.0825	
	0.0477	0.0116	40 ± 0.1	0.0853	
Fluorene	0.0165	0.0117	20 ± 0.1	0.910	
	0.0247	0.0109	20 ± 0.1	0.765	23.5
	0.0297	0.00885	20 ± 0.1	0.699	
	0.0177	0.0109	30 ± 0.1	3.48	
	0.0203	0.00935	30 ± 0.1	3.00	
2-Nitrofluorene	0.0150	0.0139	30 ± 0.1	0.228	21.0
	0.0283	0.0112	30 ± 0.1	0.267	
	0.0168	0.0112	40 ± 0.1	0.717	

The observed rates satisfy the previously proposed rate equation[2] and the electron-withdrawing group (nitro) retards the reaction, as in the oxidation of toluenes.[2] Therefore, it is probable that an analogous mechanism is operating in the oxidation of these compounds, *i.e.*, an attack of two molecules of chromium trioxide on a molecule of naphthalene or fluorene. Since practically no carbon dioxide is liberated in the oxidation of naphthalenes, a possible mechanism seems to be

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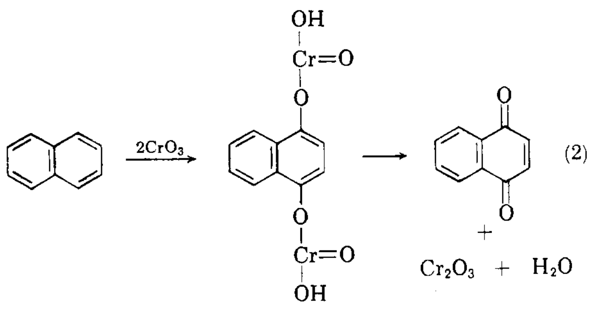
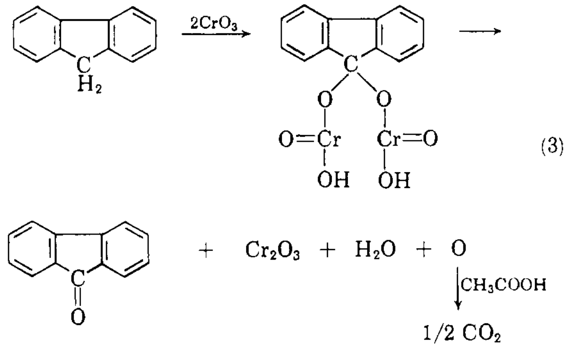
[1] R. Slack and W. A. Waters, *J. Chem. Soc.*, 1666 (1948); 599 (1949).

[2] Y. Ogata, F. Fukui, and S. Yuguchi, *J. Am. Chem. Soc.*, 74, 2707 (1952).


(2)

while the mechanism for the oxidation of fluorenes may be


(3)

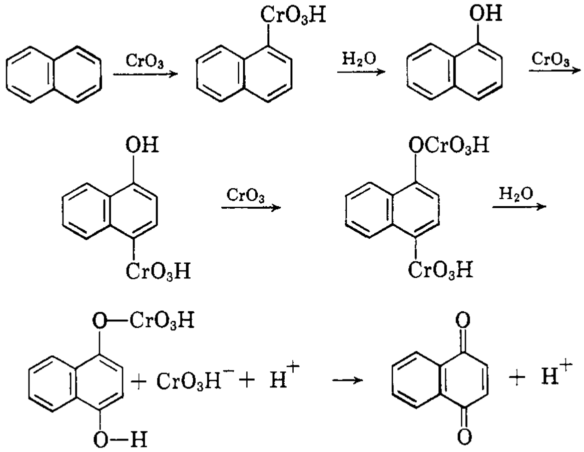
because about one half mole of carbon dioxide was liberated by the consumption of two moles of chromium trioxide (Table III). Vacuum distillation of the oxidation mixture with fluorene gave a distillate containing no hydrogen peroxide or peracetic acid. Hence there is no possibility of the production of these peroxides from the oxygen atom produced. No appreciable effect on the rate was observed on addition of 0.002–0.003 mole/l. of benzoyl peroxide or 1,3,5-trinitrobenzene, and hence, the oxidation probably involves no free radical intermediate. Ionic mechanisms have been suggested by Levitt[3] for the general oxidation in acidic solutions.

TABLE III

AMOUNT OF CARBON DIOXIDE LIBERATED DURING THE OXIDATION OF FLUORENES

	CrO_3 (*M*)	Fraction of CrO_3 Consumed	Calcd. CO_2, Mg.	Found CO_2, Mg.
Fluorene	4.97×10^{-4}	0.66	3.6	3.1
	7.49	0.78	6.4	5.7
	4.28	0.76	3.6	3.3
2-Nitro-fluorene	3.28	0.79	2.9	2.3
	7.72	0.83	7.0	5.8

An application of the Levitt mechanism[3] to the reaction seems to be less probable, since very little water is present in the reaction mixture, neither naphthol nor its derivative was detected as an intermediate, and the rate shows the second-order dependency on chromium trioxide concentration.



As is obvious from Table II, the rate constants decrease with increasing initial concentration of naphthalene and of fluorene. This phenomenon may be due to π-complex formation between chromium trioxide and aromatic compound, which results in a decrease of the actual concentration of chromium trioxide and/or a decrease of the acidity of solution. But this could not be confirmed by spectrophotometry because of the strong absorption under the experimental conditions. On the other hand, a slight increase in the rate constants was observed with increasing initial concentration of nitronaphthalene and nitrofluorene, which perhaps is due to an increase in the acidity of the solution.

The enthalpies of activation for fluorene and 2-nitrofluorene are larger than those for the other chromic acid oxidations, *e.g.*, 12.6 and 15.2 kcal./mole for benzaldehyde[4] and diphenylmethane,[5] respectively.

EXPERIMENTAL

Materials. All melting points of materials agreed with those in literature. 2-Nitrofluorene, m.p. 156,° was prepared by the nitration of fluorene.[6]

Oxidation products. The oxidation products of naphthalene and fluorene were found to be 1,4-naphthoquinone,[7] m.p. and mixed m.p. 123,° and 9-fluorenone,[8] m.p. and mixed m.p. 82°. 2-Nitrofluorene was oxidized to 2-nitro-9-fluorenone, m.p. 218° and lit.[9] m.p. 218.5.°

An example of the oxidations. A solution of chromium trioxide (10 g.) in acetic acid (60 ml.) was added with stirring to a solution of naphthalene (2 g.) in acetic acid (20 ml.) and the mixture was kept at room temperature for about 3 days. The resulting solution was poured into water (1 l.), allowed to stand for 2 hr. and filtered. The residue was washed with water and dried. The yield was 0.65 g. (26%). The crude product was recrystallized from acetic acid and methanol, giving pure product melting at 123°, 0.58 g.

Procedure for the rate measurements and the estimation of carbon dioxide. The rates were measured by iodometry as used

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(3) L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955).

(4) K. B. Wiberg, *J. Am. Chem. Soc.*, **80**, 3027 (1958).

(5) K. B. Wiberg and R. J. Evans, *Tetrahedron*, **8**, 313 (1960).

(6) W. E. Kuhn, *Org. Syntheses*, **Coll. Vol. II**, 447 (1948).

(7) C. E. Groves, *Ann.*, **167**, 357 (1873).

(8) R. Fittig and A. Schmidt, *Ann.*, **193**, 141 (1878).

(9) F. Ullmann and E. Mallet, *Ber.*, **31**, 1696 (1898).

for the oxidation of toluenes.[2] In the oxidation of naphthalene and 1-nitronaphthalene no carbon dioxide was detected by testing with a solution of barium hydroxide. The determination of the amount of carbon dioxide, evolved during the oxidation of fluorenes, was carried out as follows. The carbon dioxide was swept out by passing dry oxygen-free nitrogen gas. After having been freed of acetic acid with *o*-chloroaniline and of water with calcium chloride, the carbon dioxide was absorbed by two potash bulbs containing 40% aqueous potassium hydroxide. The increase in weight of the potash bulbs corresponds to that of the carbon dioxide liberated.

DEPARTMENT OF INDUSTRIAL CHEMISTRY
FACULTY OF ENGINEERING
KYOTO UNIVERSITY
KYOTO, JAPAN

A Novel Alkaline Rearrangement in the Naphthalene Series

D. C. MORRISON

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During work in this laboratory on β-substituted naphthalenes, it was decided to attempt to carry out nucleophilic displacement reactions on 2,3-dinitronaphthalene with alkoxides. It was observed that an excess of sodium methoxide in methanol gave, as main product, a compound different from 3-nitro-2-methoxynaphthalene. Further study showed that a nitromethoxynaphthalene had been formed, and it was finally proved by direct comparison to have been 3-nitro-1-methoxynaphthalene. Thus, a rearrangement as well as a displacement had occurred, though the mechanism of this change has not, at present, been demonstrated. It is evidently an addition to the group of cine-substitutions.[1]

Employment of dilute methoxide solution, in a slow reaction, gave some of the 3-nitro-2-methoxynaphthalene, presumably by direct displacement. This isomer can be made the main product, but it is always accompanied by some of the 3-nitro-1-methoxynaphthalene. As the purified 3-nitro-2-methoxynaphthalene did not undergo rearrangement when heated with sodium methoxide solution, simple displacement did not precede rearrangement.

Sodium or potassium hydroxides in methanol also caused the rearranged 3-nitro-1-methoxy compound to form, and the presence of water in the solvent did not prevent the reaction. Higher primary alcohols with potassium hydroxide also reacted with 2-3-dinitronaphthalene to form 3-nitro-1-alkoxynaphthalenes, but at a slower rate than with methanol. Stirring of 2,3-dinitronaphthalene with aqueous potassium hydroxide in the absence of alcohols for twenty-four hours did not give a nitronaphthol but a little unidentified, acidic and perhaps polymeric product.

Authentic 3-nitro-1-naphthol and its methyl ether were prepared from 1-3-dinitronaphthalene by methods described in the literature[2,3] The mixed melting point and infrared spectra of the samples of nitro ether from the two sources were the same.

The 3-nitro-2-methoxynaphthalene was separated from its isomer by crystallization from hexane and from aqueous acetone, and eventually had the same melting point as that given by Woodcock and Clifford.[4] It was hydrolyzed and reduced to 3-amino-2-naphthol, which was also obtained from commercial 2,3-dihydroxynaphthalene by partial amination by Friedlander's method.[5] The infrared spectra of the two preparations were identical.

The fact that 3-nitro-2-methoxynaphthalene can be formed in the reaction would seem to indicate that, in spite of the lower 2,3 bond-order in naphthalene, sufficient activation of one nitro group by the other occurs so that ordinary nucleophilic displacement takes place. Previous efforts in this direction with 3-nitro-2-bromonaphthalene have not succeeded.[6]

Further work on nucleophilic displacements of 2,-3-dinitronaphthalene is being done.

EXPERIMENTAL

Melting points are uncorrected and were taken on a Fisher-Johns block.

Reaction with rearrangement. A solution of 20 g. of sodium methoxide (0.37 mole) in 250 ml. of methanol was treated with 7.5 g. of 2,3-dinitronaphthalene (0.034 mole) with cooling. The mixture was kept in a bath with internal temperature of 45° with stirring for 11 hr. It was then cooled and treated with 1 l. of ice water and kept overnight. The product was filtered, washed with water, and dried. The yield was 6.6 g. or 94.6%. In another run, with 56 g. of sodium methoxide in 700 ml. of methanol, treated with 14 g. of dinitronaphthalene, the mixture was stirred for 4 hr. at 40–45°. The yield was 12.62 g. or 96.8%.

The reaction in methanol with potassium hydroxide was best carried out below room temperature for 1–2 days and yields were poorer than above. By-products were alkali-soluble and seemed to consist of acidic polymers.

After several recrystallizations from aqueous methanol, the 3-nitro-1-methoxynaphthalene had m.p. 103–104°, which was not depressed when mixed with an authentic sample.[2] The infrared spectra of the two samples were identical.

Cleavage of 3-nitro-1-methoxynaphthalene. A solution of 5 g. of the methyl ether in 35 ml. of acetic acid was mixed with 15 ml. of 48% hydrobromic acid and then refluxed for 27 hr. The solution was cooled and diluted with 0.5 l. of water. After 2 hr., the solid was filtered and washed, and then extracted repeatedly with dilute sodium carbonate solution until the extracts were no longer red. The combined dark red extracts were acidified with hydrochloric acid and the

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