

means of equation 2, was 11,370 cal./mole and the entropy of vaporization was 38.14 cal./deg. mole. Because of the low vapor pressure (7.65 mm.) at 298.16°K. and the lack of other pertinent data, a gas imperfection correction was not estimated; however, a correction for entropy of compression

was included. The results of the calculations are summarized in Table IV.

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[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

The Relative Rates of Chromic Acid Oxidation of Toluenes in Acetic Acid

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The rates of oxidation of toluene and ring-substituted toluenes by chromium trioxide in acetic acid at 70° have been estimated iodometrically. The rates are first-order with respect to the concentration of toluenes and second-order with respect to that of chromium trioxide. Chromic acetate produced exhibits a retarding action which is probably due to its ability to decrease the acidity of the medium. In general, electron-attracting groups in the benzene ring diminish the rate in the order: None > *p*-Br > *p*-Cl > *p*-CN > *p*-NO₂. The above results are explicable by a tentative mechanism which involves a rate-determining attack of two molecules of chromium trioxide and a subsequent elimination of chromic oxide from the intermediate with or without an attack of other molecules of chromium trioxide. In the latter case, carbon dioxide is evolved probably as a result of an induced oxidation. The rate constants tend to decrease with increased initial concentration of toluenes.

Kinetic studies on the chromic acid oxidation of ethanol,¹ isopropyl alcohol² and carboxylic acids³ in aqueous media, and of aromatic aldehydes⁴ in a mixture of acetic acid and sulfuric acid⁴ have been reported. Slack and Waters⁵ have observed, in the initial reaction of chromic acid oxidation of diphenylmethane in acetic acid, that the rate is first-order with respect to diphenylmethane and second-order with respect to chromium trioxide, the rate being retarded by the presence of chromic acetate or water. But little appears to have been reported regarding the oxidation of toluene.

The present paper deals with a kinetic investigation upon the oxidation of toluene and ring-substituted toluenes in acetic acid with chromium trioxide. Rates were estimated iodometrically. A characteristic feature of this reaction is the retardation by chromic acetate and the induced oxidation producing carbon dioxide the amount of which was also measured.

Experimental

Materials.—Glacial acetic acid was rectified by successive distillations from chromium trioxide added with acetic anhydride and then from chromium trioxide alone.⁶ It was

free from oxidizable substances and water, m.p. 16.6°. Chromium trioxide was of best grade free of sulfate and chloride, its purity of 100% being confirmed iodometrically. Toluene and substituted toluenes were purified by duplicate distillations; those which were solid exhibited melting points in agreement with the literature and those which were liquid showed constant boiling points. About 20% of chromium trioxide was reduced during its solution in acetic acid at 60° for about eight hours. Therefore, it was necessary to determine the amount of chromic acetate from the difference between the dissolved weight of chromium trioxide and the amount found by the iodometric titration of the solution. In general, the concentration of the chromium trioxide solution was ca. 0.4 mole/l.

Apparatus and General Procedure.—In one glass-stoppered erlenmeyer flask was placed 10 cc. of the solution of chromium trioxide and in the other a solution of toluene in acetic acid. The two flasks were dipped in an electrically-controlled thermostat maintained at 70.0 ± 0.1°. After reaching the temperature equilibrium, 5 cc. of the solution of toluene was added to the solution of chromium trioxide. One-cc. aliquots were pipetted out at known intervals of time and titrated with 0.05 *N* thiosulfate after being added to 5 cc. of 10% aqueous sulfuric acid and 3 cc. of 25% aqueous potassium iodide. The pipets were calibrated at the temperature.

The determination of the amount of carbon dioxide, evolved by the induced oxidation and identified as barium carbonate, was carried out as follows. In a flask equipped with a ground-glass reflux condenser and dipped in a thermostat at 70°, an acetic acid solution of chromium trioxide was mixed with that of toluene. The carbon dioxide was drawn out by passing air, which is free of oxygen, with alkaline hydrosulfite solution and carbon dioxide with solid potassium hydroxide. After being freed of acetic acid with aniline and of water with calcium chloride, the carbon dioxide was absorbed by 40% aqueous caustic potash. The increase in weight of the potash bulb corresponds to that of carbon dioxide liberated. The reliability of this procedure was proved by a test with a known amount of carbon dioxide produced from calcium carbonate and hydrochloric acid. If oxygen in the air or a trace of acetic anhydride in the acetic acid was not removed, a little larger amount of carbon dioxide was produced. The final concentration of chromium trioxide was consistent with that expected from the kinetic data. The decrease in chromium trioxide content with pure acetic acid was calculated by the weight of carbon dioxide, which was in agreement with that observed in the kinetic experiment. No carbon dioxide was detected by employing water in place of acetic acid as solvent.

The ether extracts of the oxidation products of toluene and *p*-nitrotoluene gave benzoic acid, m.p. and mixed m.p. 122–123°, and *p*-nitrobenzoic acid, m.p. and mixed m.p. 239–240°, respectively. No indication of the other product was observed.

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(4) E. Lucchi, *Boll. sci. facoltà chim. ind. Bologna*, 208 (1940); 333 (1940); 165, 176 (1941); *Gazz. chim. ital.*, **71**, 729, 752 (1941) [*C. A.*, **36**, 8880 (1942); **37**, 2252 (1943); **37**, 4293 (1943); **36**, 7012 (1942)].

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(6) For the purification of acetic acid see K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 960 (1924); 983 (1927); A. Weissberger and E. Proskauer (translated by R. G. A. New), "Organic Solvents," Clarendon Press, Oxford, 1935, p. 146.

Calculation and Results.—The rate constants were calculated graphically by means of an equation, *i.e.*, the modified Slack-Waters equation for diphenylmethane⁵

$$dx/dt = \kappa \{a - (x_0/g)\} \{b - x\}^2 \{b - x - (y/h)\} \quad (1)$$

where *a* is the initial concentration of toluene (moles/l.), *b* that chromium trioxide, *x* the decreased concentration of chromium trioxide after *t* seconds, *x*₀ the corrected *x* in which the oxidation of the solvent is considered,⁷ *y* the concentration of chromic acetate, *i.e.*, *x* plus initial concentration of chromic acetate, and *g* and *h* are constants. The rate constants thus calculated are given in Table I together with the appropriate values of *g* and *h* determined experimentally. Table II shows the data on carbon dioxide estimation, where the theoretical weight of carbon dioxide is calculated from equations (1) and (3) to be 64 mg.

TABLE I

THE RATES OF THE OXIDATION OF TOLUENES IN ACETIC ACID AT 70 ± 0.1°

Substituent	<i>a</i> mole/l.	<i>b</i> mole/l.	$\kappa \times 10^2$ (mole/l.) ⁻³ sec. ⁻¹
None	0.1575	0.2670	42.9 ± 1.9 ^a
<i>g</i> = 4	.1080	.2670	51.5 ± 1.5
<i>h</i> = 4	.0684	.2670	65.8 ± 1.6
	.0690	.2760	65.1 ± 1.5 ^b
<i>p</i> -Br	0.1468	0.2935	29.0 ± 2.1
<i>g</i> = 4	.0735	.2760	44.2 ± 1.1
<i>h</i> = 4	.0368	.2760	49.9 ± 2.2
<i>p</i> -Cl	0.0729	0.2915	26.7 ± 0.8
<i>g</i> = 4	.0364	.2945	28.2 ± .5
<i>h</i> = 4			
<i>p</i> -CN	0.1252	0.2535	7.35 ± 0.27
<i>g</i> = 2	.0762	.2535	8.67 ± .35
<i>h</i> = 2	.0626	.2535	9.06 ± .39
<i>p</i> -NO ₂	0.1458	0.2915	5.21 ± 0.07
<i>g</i> = 2	.0740	.2915	5.61 ± .11
<i>h</i> = 2	.0361	.2915	6.72 ± .07
<i>m</i> -NO ₂	0.2770	0.2770	4.72 ± .08
<i>g</i> = 2	.0693	.2770	7.51 ± .12
<i>h</i> = 2			
<i>o</i> -Cl	0.0632	0.2535	13.4 ± 0.4
<i>g</i> = 4			
<i>h</i> = 10			
<i>o</i> -CN	0.0765	0.2641	6.00 ± 0.66
<i>g</i> = 4			
<i>h</i> = 4			
<i>o</i> -NO ₂	0.0923	0.2770	5.56 ± 0.18
<i>g</i> = 4			
<i>h</i> = 4			

^a Figures following ± indicate probable errors. ^b Toluene with additional 0.0054 mole/l. chromic acetate.

TABLE II

THE AMOUNT OF CARBON DIOXIDE LIBERATED DURING THE OXIDATION OF TOLUENES

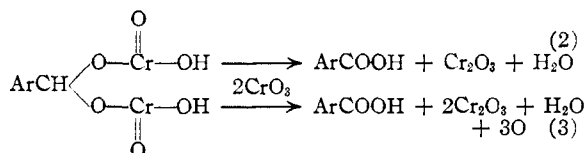
Temp., 70 ± 0.1°; time, 160 min.; vol. of the solution, 25 cc.; *a*, 0.0624 *M*; *b*, 0.2495 *M*; initial concn. of Cr(CH₃COO)₃, 0.0364 *M*.

	CO ₂ , mg.	Substituent	CO ₂ , mg.
Without toluene	6	<i>p</i> -NO ₂	5
Substituent		<i>m</i> -NO ₂	6
None	50	<i>o</i> -Cl	48
<i>p</i> -Br	53	<i>o</i> -CN	43
<i>p</i> -Cl	51	<i>o</i> -NO ₂	46
<i>p</i> -CN	8		

(7) The concentration of chromium trioxide in this acetic acid (initial concn., 0.2770 mole/l.) at 70° decreased almost linearly in such a conversion as 0.24% at 10 min. and 2.22% at 80 min. Hence the term involving the rate of the oxidation of solvent was neglected in equation (1). The same reasoning may be applied to the oxidation of benzoic acid at least in initial stages.

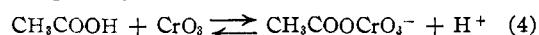
Discussion of Results

The rate equation is complicated because of the acid-catalyzed reaction. If the term $\{b - x - (y/h)\}$ representing the acidity of the solution is eliminated, the rate is first-order with respect to toluene and second-order to chromium trioxide; therefore, the attack of two molecules of chromium trioxide on a molecule of toluene seems to be involved, as Slack and Waters have suggested.⁵ The rates for the oxidation of *p*-substituted toluenes decrease in the order⁸: None > Br > Cl > CN > NO₂, *i.e.*, the rate diminishes as the electron density in the methyl carbon falls. Thus 2,4-dinitrotoluene was inactive to the oxidation under these conditions. Consequently, it is probable that a rate-determining combination of cationoid chromium atoms of chromium trioxide with a methyl carbon atom, just as in the chromyl chloride addition,⁹ followed by a rapid rearrangement forming oxygen-carbon bonds occurs. As a tentative mechanism, the authors assume that the produced intermediate then reacts rapidly by the following two processes.



The route (2) corresponds to those cases where the value of *g* in equation (1) is equal to 2 (*m*-nitro, *p*-nitro or *p*-cyanotoluene) and no carbon dioxide is detected, if the correction for the oxidation of the solvent itself was taken into account (Table II). On the other hand, route (3) seems to be applied to those toluenes which have a *g* value of 4 (toluene, *o*-halogeno-, *p*-halogeno-, *o*-cyano- or *o*-nitrotoluene), requiring four moles of active chromium trioxide for the oxidation of one mole of the toluenes. This oxidation is related to the evolution of 1.01–1.24 moles (theoretically, 1.5 moles) of carbon dioxide, which might be a product of the induced oxidation of the solvent by the active oxygen formed in equation (3).

The reaction is evidently subject to acid catalysis, for the addition of a small amount of sulfuric acid markedly accelerates the reaction. Although no absolute accurate value of *pH* could be obtained, our results of its measurement with acetic acid solutions of chromium trioxide (*e.g.*, 0.267 *M* solution containing 0.066 *M* chromic acetate) by means of a glass electrode at 21° show that the solutions have much larger acidity than pure acetic acid *via* the protolytic reaction such as



Increasing the concentration of chromic acetate and concurrently decreasing that of chromium trioxide by the reaction with toluene produces a decrease in the acidity, which finally drops even below that of pure acetic acid when the amount of chromic

(8) Since the value of *g* or *h* is different with each toluene derivative, the rate constants of these toluenes do not obey this order as Table I shows. But if the consumptions of chromium trioxide at definite *t*, *a* and *b* are compared, the decrease in this order is apparent.

(9) M. A. Étard, *Ann. chim. phys.*, **22**, 218 (1881).

