concentrating the volume to about 400 ml. on a steam cone. The red-colored solution was filtered and placed in refrigerator for 2 days. The bright yellow crystals were filtered off and washed with ether. The product melted at 208–210°.

*Anal.* Calcd. for $C_{20}H_{13}N_3O_9S$: C, 50.96; H, 2.78; N, 8.91. Found: C, 51.06; H, 2.97; N, 8.80.

Infrared spectrum of V: 6.26 (m), 6.56 (s), 7.28 (s), 7.46 (s), 7.64 (shoulder), 8.42 (m), 8.51 (s), 9.20 (broad, m), 10.03 (m), 10.48 (m), 10.97 (m), 11.41 (m), 11.72 (s), 11.88 (w), 12.33 (broad, s), 13.08 (m), 13.22 (w), 13.62–13.76 (broad, m), 14.47 (w).

**Acetolysis of 2,4,7-Trinitro-9-fluorenyl *p*-Toluenesulfonate.**—A solution containing 2.4 g. of V in 80 ml. of glacial acetic acid was refluxed for 19 hr. On cooling, 1.7 g. (93%) of VI separated. The product melted at 240–242° alone and 241–242° when mixed with authentic VI.

**2,4,7-Trinitro-9-fluorenyl Acetate (VI)** was prepared by gently refluxing 3.3 g. (0.01 mole) of III in 80 ml. of glacial acetic acid for 2 hr. The solution was cooled to room temperature yielding a light yellow precipitate which was filtered and washed with 95% ethanol. The air-dried product was further dried in a drying oven at 80–90° yielding 3.1 g. (85%) of acetic acid-free product melting at 235° with decomposition. Recrystallization from acetone raised the melting point to 240–242°.

*Anal.* Calcd. for $C_{15}H_9N_3O_8$: C, 50.15; H, 2.52; N, 11.70. Found: C, 50.02; H, 2.57; N, 11.78.

Infrared spectrum of VI: 5.74 (s), 6.21–6.24 (split, m), 6.55 (s), 7.46 (s), 7.62 (m), 8.16–8.26 (split, s), 9.22 (m), 9.55 (m), 11.00 (w), 11.22 (m), 11.84 (broad, w), 12.04 (w), 12.22 (m), 13.02 (w), 13.37 (s).

**Formolysis of 2,4,7-Trinitro-9-fluorenyl *p*-Toluenesulfonate.**—Heating 0.5 g. of V in 20 ml. of formic acid (99–100%) for 17 hr. under reflux yielded 0.35 g. (96%) of VII, melting at 232–235°. Mixed melting point with authentic VII was 232–234°.

**2,4,7-Trinitro-9-fluorenyl Formate (VII).**—A mixture of 3.3 g. (0.01 mole) of III in 50 ml. of formic acid (98–100%) was refluxed for 2 hr. Upon cooling, yellow crystals separated out, which were filtered and washed with alcohol. The dried product melted at 234° dec. and weighed 3.3 g. (95%). Recrystallization from acetone did not raise the melting point.

*Anal.* Calcd. for $C_{14}H_7N_3O_8$: C, 48.71; H, 2.04; N, 12.17. Found: C, 48.71, 49.10; H, 1.66, 2.16; N, 11.99, 12.28.

Infrared spectrum of VII: 5.76 (s), 6.18 (m), 6.24 (m), 6.50–6.56 (split, s), 7.42 (s), 7.62 (m), 8.36 (m), 8.50 (w), 8.78–8.86 (split, s), 9.12 (m), 9.22 (m), 9.86 (w), 10.28 (w), 10.66 (m), 10.73 (m), 11.10 (s), 11.65 (m), 12.11 (s), 12.80 (w), 12.98 (w), 13.46 (s).

**9-Bromo-2,4,7-trinitrofluorene (VIII).**—To a mixture of 6.6 g. (0.02 mole) of III in 60 ml. of nitromethane and 150 ml. of diethyl ether, was introduced 35 ml. of aqueous hydrogen bromide (48%). The reaction mixture was refluxed gently for 2.5 hr. with stirring. The cooled solution was filtered and stored in the refrigerator overnight. The yellow crystalline product was collected by suction filtration and washed with small portions of cold ether. Recrystallization of dried material from nitromethane–ether gave 5.4 g. (70.5%) of VII melting at 179–180°.

*Anal.* Calcd. for $C_{13}H_6N_3O_6Br$: C, 41.07; H, 1.59; N, 11.06. Found: C, 41.42; H, 1.86; N, 11.36.

Infrared spectrum of VIII: 6.20 (w), 6.27 (m), 6.48 (s), 6.59 (s), 7.48 (s), 7.66 (m), 8.43 (w), 8.62 (w), 8.85 (w), 9.20 (m), 10.80 (w), 10.97 (m), 11.10 (w), 11.76 (m), 12.11 (w), 12.28 (s), 12.80 (w), 13.06–13.14 (broad, m), 13.64 (s), 14.18 (w).

**Isolation of Crystalline Molecular Complexes.**—Approximately equimolar amounts of donor and acceptor compounds were dissolved separately to near saturation in the appropriate solvent at its boiling point. Upon mixing together, deeply colored solutions were obtained. After cooling overnight, the crystalline complexes were collected by filtration, washed with small portions of anhydrous ether, and dried. For complexes of 2,4,7-trinitro-9-fluorenyl acetate, glacial acetic acid solvent was used in all cases. Nitromethane solvent was used in the preparation of all of the 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate complexes with the exception of that with phenanthrene.

The *p*-toluenesulfonate–phenanthrene complex was formed when 500 ml. of hot glacial acetic acid solution of 0.05 g. of the *p*-toluenesulfonate and 5.40 g. of phenanthrene was allowed to stand for several days at room temperature. The bright yellow needles were filtered, washed with small portions of cold acetic acid, and air-dried. The melting points and nitrogen analyses for the six complexes prepared are listed in Table II.

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# Multiple Substituent Effects in the Solvolysis and Thiosulfate Reactions of 4-Substituted α-Chloro-3-nitrotoluenes

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The rates of reaction of a series of 4-substituted α-chloro-3-nitrotoluenes with thiosulfate do not fall on the U-shaped curve for the 4-substituted α-chlorotoluenes, but describe a separate U-shaped curve. The rates of solvolysis of both series in 50% ethanol are satisfactorily correlated with $\sigma^+$ up to values of 0.2. At more positive values of the substituent constant rates are better correlated with ordinary $\sigma$ values. The two branches of the solvolysis plot are suggestive of a carbonium ion mechanism and a bimolecular attack of solvent, respectively.

Large deviations from the Hammett equation have generally been recorded[1] for reactions of benzyl halides (3- and 4-substituted α-halotoluenes) with anions.[1,2] Plots of log *k vs.* sigma for these reactions are, in general, U- or J-shaped. Similar behavior has been observed in the solvolysis of a series of benzoyl halides.[3] It has been known for

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(1) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(2) R. Fuchs and A. Nisbet, *J. Am. Chem. Soc.*, **81**, 2371 (1959).

(3) E. Crunden and R. F. Hudson, *J. Chem. Soc.*, 501 (1956), and preceding papers.

some years that the two branches of the Hammett plot do not result from grossly different mechanisms; in a number of cases second-order kinetics have been established throughout a series. In general the unsubstituted benzyl compound shows the minimum rate[4] in the *p*-substituted series, although a variety of nucleophiles,[1,2] solvents,[2] and ionic strengths,[5] have been employed. Swain[6] has discussed the origin of the rate minimum in these reaction series in terms of two types of bimolecular, nucleophilic displacement reactions: in one, the benzylic carbon atom becomes more negative as the "tight" transition state is attained from the initial state (with bond formation tending to proceed to a greater degree than bond rupture), and this reaction is facilitated by electron-withdrawing substituents; in the second type the benzylic carbon atom becomes more positive as the "loose" transition state is attained (with bond rupture exceeding bond formation), and this reaction is aided by substituents to an extent dependent on their electron-releasing abilities.

The present study was undertaken to establish whether, within the limitation of the U-shaped Hammett plot, the sum of the sigma values for *m*- and *p*-substituents is a reliable indication of the $S_N2$ reactivity of 3,4-disubstituted α-chlorotoluenes. As a comparison the solvolytic reactivities have also been examined.

## Results

A series of five *p*-substituted *m*-nitrobenzyl chlorides (α-chloro-4-methoxy-3-nitrotoluene, α-chloro-3-nitro-*p*-xylene, α-chloro-3-nitrotoluene, α,4-dichloro-3-nitrotoluene, and α-chloro-3,4-dinitrotoluene) were prepared. Rates of reaction with sodium thiosulfate in 60% acetone at 30° (Table I) and rates of solvolysis in 50% ethanol at 60° (Table II) have been determined.

Table I

Rates of Reaction of 4-Substituted α-Chlorotoluenes and of 4-Substituted α-Chloro-3-Nitrotoluenes with Thiosulfate in 60% Acetone at 30°

| 4-Substituent | 3-Substituent | $k^a$ | $\sigma_{3,4}{}^b$ |
|---|---|---|---|
| $CH_3$ | H | 6.68 | −0.170 |
| *i*-$C_3H_7$ | H | 5.16 | − .151 |
| H | H | 4.27 | .000 |
| Cl | H | 6.10 | + .227 |
| $NO_2$ | H | 10.9 | + .778 |
| $OCH_3$ | $NO_2$ | 10.8 | + .414 |
| $CH_3$ | $NO_2$ | 6.00 | + .505 |
| H | $NO_2$ | 5.98 | + .710 |
| Cl | $NO_2$ | 9.45 | + .901 |
| $NO_2$ | $NO_2$ | 20.0 | +1.379 |

[a] Second-order rate constants (l. mole$^{-1}$ sec.$^{-1}$) × $10^3$. All values are averages of two or more determinations. At time of mixing ($S_2O_3^=$) = 0.04 *M*, (RCl) = 0.025 *M*. Stated temperature regulated to ±0.02°. Solvent is 40% water + sufficient acetone to make up total volume. [b] Combined sigma value for 3- and 4-substituents, experimentally determined (ref. 1).

Table II

Rates of Solvolysis of 4-Substituted α-Chlorotoluenes and 4-Substituted α-Chloro-3-Nitrotoluenes in 50% Ethanol at 60°

| 4-Substituent | 3-Substituent | $k^a$ | $\Sigma\sigma^{+\,b}$ or $\sigma_{3,4}{}^c$ |
|---|---|---|---|
| $CH_3$ | H | 27.3 | $-0.311^b$ |
| *i*-$C_3H_7$ | H | 17.2 | $-\ .280^b$ |
| H | H | 3.02 | $.00^b$ |
| Cl | H | 1.69 | $+\ .114^b$ |
| $NO_2$ | H | 0.198 | $+\ .778^c$ |
| $OCH_3$ | $NO_2$ | 6.05 | $-\ .07^b$ |
| $CH_3$ | $NO_2$ | 0.437 | $+\ .505^c$ |
| H | $NO_2$ | .231 | $+\ .710^c$ |
| Cl | $NO_2$ | .183 | $+\ .901^c$ |
| $NO_2$ | $NO_2$ | .0726 | $+1.379^c$ |

[a] First-order rate constants (sec.$^{-1}$) × $10^5$. All values are averages of two or more determinations. At time of mixing (RCl) = 0.005 *M*. Stated temperature regulated to ±0.02°. Solvent is 50% commercial absolute ethanol-50% water by volume. [b] Sum of $\sigma_m{}^+$ and $\sigma_p{}^+$ values of H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958). [c] Table I, footnote *b*.

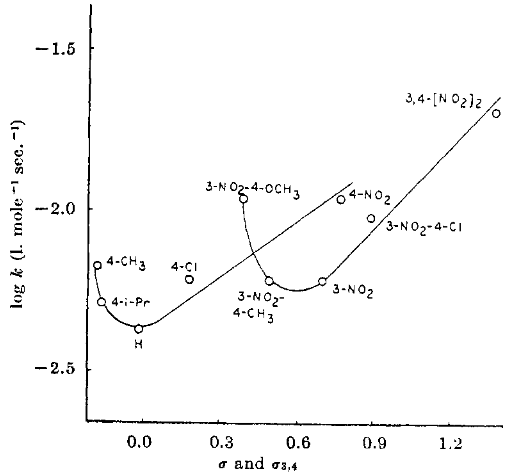

Fig. 1. Rates of reaction of 3- and 4-substituted α-chlorotoluenes with thiosulfate in 60% acetone at 30°

## Discussion

**The Thiosulfate Reaction.**—Data from Table I are plotted in Figure 1. The possibility of strong resonance interaction with the side chain appears remote in the thiosulfate reaction, so ordinary sigma values have been used in this Hammett equation plot. The combined sigma values for 3- and 4-substituents are those reported by Jaffé, which have been experimentally determined. These values are no more than 0.04 sigma unit less positive than the algebraic sum of the individual *meta* and *para* sigma constants, except in the case of 3,4-dinitro substitution, in which the measured value is 0.11 less positive, presumably due to an appreciable steric

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[4] Various members of the benzoyl halide series may show the rate minimum in solvolysis[3] depending on solvent polarity. In the benzyl halides *m*-substituted compounds may show the rate minimum [W. T. Miller, Jr., and J. Bernstein, *J. Am. Chem. Soc.*, **70**, 4800 (1948)]; [D. M. Carlton, unpublished studies], but it is questionable whether *m* and *p*-substituted benzyl halides necessarily have the same rho value and fall on the same line. [J. Hine, *J. Am. Chem. Soc.*, **81**, 1126 (1959)].

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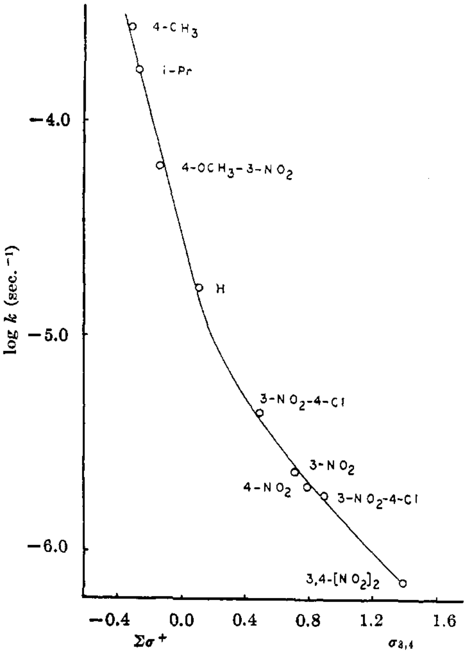

Fig. 2. Solvolysis of 3- and 4-substituted $\alpha$-chlorotoluenes in 50% ethanol

inhibition of resonance. The *p*-substituted *m*-nitrobenzyl chloride series do not fall on the curve (or extension of the curve) of the *para*-substituted series; rather, a second, entirely distinct U-shaped curve results. Thus, $\alpha$-chloro-4-methoxy-3-nitrotoluene, of the disubstituted series, most nearly resembles $\alpha$-chlorotoluene with respect to the electron density at the side chain (as estimated by sigma values), but it is one of the most reactive compounds of this series. Rather, it is the *p*-unsubstituted *m*-nitrobenzyl chloride which is the least reactive of its series. Clearly, the rates represented in Figure 1 are not a simple function of ordinary sigma values, nor are they related in any obvious way to $\sigma_{\mathrm{I}}$,[7] $\sigma_{\mathrm{R}}$,[7] or $\sigma^+$ values. Qualitatively, the *m*-nitro group appears to exercise considerably less than the usual electron-withdrawing power. There is some change in the shape of the curve; the slope (rho) of the right-hand (positive sigma) branch is somewhat greater in the *m*-nitro series. This is almost exactly the effect of decreasing the dielectric constant of the solvent[2] (45.5 for 60% acetone to 37.4 for 60% 1,2-dimethoxyethane), and presumably results from a tighter transition state in both cases.

**Solvolysis.**—The rates of solvolysis of the 4-substituted $\alpha$-chlorotoluenes and the 4-substituted $\alpha$-chloro-3-nitrotoluenes in 50% ethanol at 60° (Table II, Fig. 2) are well correlated with $\sigma^+$ values at values of up to +0.2. The straight line corresponds with a rho value of about −2.9. At sigma values greater than +0.2 a fairly straight line may be drawn *vs.* $\sigma^+$ ($\rho$ = *ca.* −0.8), or a somewhat curved line (Fig. 2) against $\sigma$. The two slopes in different substituent constant ranges suggest, respectively, a unimolecular reaction *via* the benzyl cation, and a bimolecular attack by solvent molecules at the benzylic carbon atom. The latter should proceed through a "loose" transition state under the combined influence of a weak, uncharged nucleophile, a benzylic substrate, and a strongly anion-solvating solvent. It is probably coincidental that the bimolecular reaction appears to follow $\sigma^+$ values, although in the "loose" SN2 transition state a considerable fraction of a positive charge is developed. It is also possible that the two branches of the curve represent a gradual transition from a more nearly limiting SN1 mechanism to a less nearly limiting mechanism.[8] However, a concave Hammett plot is usual in the SN2 reactions of benzyl compounds. In the range of substituent constants in question (+0.2 to +1.4) the numerical difference between sigma and $\sigma^+$ are not large and are in the same direction in all of the cases under consideration. A correlation of rates with sigma, rather than $\sigma^+$, is to be preferred, but is not here rigorously established.

It is of interest to note that a plot similar to Figure 2 can be drawn for the solvolysis benzyl tosylates in 55.6% acetone.[8] The rate reported[9] for the *p*-methoxy compound lies above the line, but the instability of this compound, the rapidity of solvolysis, and the extrapolation procedure rendered this datum considerably less certain than others of the study. Ignoring this point one may draw a straight line *vs.* $\sigma^+$ to a value of about +0.2, and at more positive values a second straight line *vs.* $\sigma^+$ or a slightly curved line *vs.* $\sigma$ with no point falling more than about 0.03 sigma unit from the lines. While this does not disprove the contention[8] that the benzyl tosylate solvolyses occur by (a spectrum of) SN1 mechanisms, it does not lend strong support to the disproof of the "two mechanism" concept of solvolysis.

**Combined $\sigma$ Values.**—A number of combined sigma values for two or more substituents have been experimentally determined.[1] These are available for all of the 3-nitro-4-substituent combinations used herein. Although the combined values of interest are not greatly different from the sum of the individual values, the difference is generally in the direction consistent with a partial steric inhibition of resonance. In the present work no correction has been applied to the sum of the individual $\sigma^+$ values, although a correction may be appropriate on the premise that inhibition of resonance should be at least as significant (and probably more so) when $\sigma^+$ is appropriate.

## Experimental

**Reagents.**—The purification of solvents and of several monosubstituted $\alpha$-chlorotoluenes has been described previously.[2] A commercial sample of $\alpha$-chloro-*m*-nitrotoluene

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[8] G. S. Hammond, C. E. Reader, F. T. Fang, and J. K. Kochi, *J. Am. Chem. Soc.*, **80**, 568 (1958).

[9] J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3445 (1953).

was recrystallized from heptane, (m.p. 45.4–46.0°). Commercial α,3,4-trichlorotoluene was fractionally distilled (b.p. 71° at 1 mm.). The chloromethylation procedure[10] was used in the preparation of α-chloro-4-methoxy-3-nitrotoluene, m.p. 87.0–87.6° (reported,[10] m.p. 85–86°).

**α-4-Dichloro-3-nitrotoluene.**—Commercial 4-chloro-3-nitrobenzaldehyde was reduced with sodium borohydride in aqueous dioxane to 4-chloro-3-nitrobenzyl alcohol, m.p. 63–64°.

*Anal.* Calcd. for $C_7H_6ClNO_3$: C, 44.8; H, 3.20. Found: C, 44.8; H, 3.34.

The alcohol was converted with thionyl chloride to the chloride, which was distilled in a Hickman still at 0.05 mm. at a bath temperature of 85° ($n^{30}\mathrm{D}$ 1.5805).

*Anal.* Calcd. for $C_7H_5Cl_2NO_2$: C, 40.8; H, 2.43; Cl, 34.5. Found: C, 40.8; H, 2.38; Cl, 33.7.

**α-Chloro-3,4-dinitrotoluene.**—Commercial 3,4-dinitrotoluene was oxidized to 3,4-dinitrobenzoic acid,[11] and the latter was converted to the acid chloride using thionyl chloride. Sodium borohydride reduction of the acid chloride in 1,2-dimethoxyethane solution at 10° gave a low yield of impure 3,4-dinitrobenzyl alcohol, m.p. 55.5–57.0°.

*Anal.* Calcd. for $C_7H_6N_2O_5$: C, 42.5; H, 3.03. Found: C, 40.1; H, 1.95.

Treatment of the alcohol with thionyl chloride, followed by distillation of the product in a Hickman still at 0.05 mm. pressure and a bath temperature of 90° gave α-chloro-3,4-dinitrotoluene, $n^{30}\mathrm{D}$ 1.5801.

*Anal.* Calcd. for $C_7H_5ClN_2O_4$: C, 38.8; H, 2.33; Cl, 16.4. Found: C, 39.4; H, 2.51; Cl, 16.5.

**α-Chloro-*m*-nitro-*p*-xylene.**—*p*-Tolualdehyde was nitrated[12] to give *m*-nitro-*p*-tolualdehyde, which was reduced with sodium borohydride to 4-methyl-3-nitrobenzyl alcohol, m.p. 42–43°.

*Anal.* Calcd. for $C_8H_9NO_3$: C, 57.5; H, 5.40. Found: C, 57.8; H, 5.44.

The alcohol and thionyl chloride reacted to produce α-chloro-*m*-nitro-*p*-xylene, which, after recrystallization from hexane melted at 47.0–47.8°; (reported,[13] m.p. 45°).

**Kinetic Measurements.**—The procedure used in the thiosulfate reactions is that previously described.[2] The solvolysis experiments were carried out in the following manner: in a 250-ml. volumetric flask, 125 ml. of water and approximately 115 ml. of (absolute) ethanol were thermally equilibrated at 60°. An 8-ml. sample of a solution, containing a known weight of the halogen compound (about 0.0013 mole) in ethanol was added, and ethanol was added to bring the total volume to 250 ml. Aliquots of 25 ml. were periodically withdrawn, diluted with cold water, and titrated with 0.02 *N* sodium hydroxide solution using a Sargent-Malmstadt titrator. The reactions were followed to 55–80% completion.

**Acknowledgment.**—This work was supported by National Science Foundation Grant NSF G-10033.

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# Conformational Analysis. XXVII. The Conformers of 2-Fluorocyclohexanone[1,2]

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The syntheses and physical properties including dipole moments of *cis*- and *trans*-2-fluoro-4-*t*-butylcyclohexanone are described. From the dipole moment of 2-fluorocyclohexanone it was concluded that the compound is a mixture of equatorial and axial conformers, and that the former predominates in the mixture by an amount which varies with solvent from 52% in heptane to 85% in dioxane.

Previous papers have described the conformations of 2-chlorocyclohexanone,[3] 2-bromocyclohexanone,[4] and related compounds.[5] In each case *cis*-2-halo-4-*t*-butylcyclohexanone was used as a model which was considered to have the halogen exclusively equatorial, while the *trans* isomer had the halogen exclusively axial. Using these models it was possible to measure the equilibrium point in more flexible systems by various methods, most of which had been developed earlier by other workers, including ultraviolet spectra,[6] infrared spectra,[7] polarographic reduction,[8] rotatory dispersion,[9] and especially by dipole moment measurements.[10] The present work describes similar studies with the corresponding fluoroketones.

2-Fluorocyclohexanone (I) itself has been studied by Kende,[11] who has concluded from data of the kind mentioned above that there was no substantial percentage of the axial conformer in benzene solution at 35°. Qualitative support for this sugges-

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