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(15) These cell dimensions agree well with the values reported by Z. A. Akopyan, R. L. Avoyan, and Y. T. Struchkov, *Zh. Strukt. Khim.*, **4**, 772 (1963); $a = 23.56$ Å, $b = 7.67$ Å, $c = 12.54$ Å, $\beta = 95.5°$.
(16) All calculations were carried out on an IBM 370-155 computer under the CRYM system of crystallographic programs. The quantity minimized in the least-squares calculations was $\Sigma w(F_o^2 - F_c^2)^2$, with $w = \sigma^{-2}(F_o^2)$.
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Notes

Kinetics of Hydrolysis of *o*-Tolunitrile in Moderately Concentrated Perchloric Acid Solutions[1]

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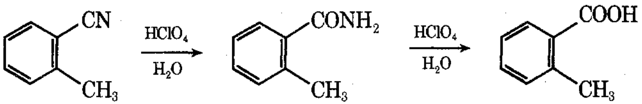
A kinetic study of the hydrolysis of benzonitrile was recently published by Hyland and O'Connor.[3] This prompts us to report a set of data obtained some years ago[4] concerning rates of hydrolysis of *o*-tolunitrile in $HClO_4$ solutions at 133.5°.

The hydrolysis reaction is represented in eq 1. An analytical technique was chosen that reveals only destruction of the nitrile and is insensitive to further hydrolysis of amide to acid. The data obtained in 1.5-6 *M* $HClO_4$ solutions are listed in Table I.



(1)

These data are correlated quite well by the linear free energy relationship (LFER) of eq 2, in which H_0 is the Hammett acidity function, k_ψ is the measured pseudo-first-order rate constant at any acid concentration, and k_2^0 is the second-order rate constant (first order in substrate, first order in H^+) at infinite dilution in water as reference state.[5] The correlation and the resulting parameters are summarized in Table II. The slope (ϕ value) is +0.61.

$$\log k_\psi + H_0 = \phi(H_0 + \log[\mathrm{H}^+]) + \log k_2^0 \qquad (2)$$

Correlation of $\log k_\psi + H_0$ with $\log a_w$,[6] where a_w is the activity of water, was also attempted. That correlation is also summarized in Table II. The slope (w value) is +3.33. As revealed particularly by the standard deviations of points from the linear regression lines, σ_y, the correlation with $\log a_w$ is less satisfactory than with (H_0 + log [H^+]). A plot of the correlation with $\log a_w$ shows slight but persistent curvature, whereas the LFER plot is straight except for small random deviations most likely due to experimental error.

Correlation of $\log k_\psi$ with $-H_0$[7] was also attempted, and the correlation is summarized in Table II. The σ_y values show that this correlation gives the least satisfactory fit of experimental points to a straight line. The slope is 0.55.

The H_0 values[8] and $\log a_w$ values[6] employed in these correlations are for 25° or thereabouts, while the reactions were conducted at 133.5°. Also, acid concentrations were not corrected for thermal expansion of the reaction solutions from room to reaction temperature. The magnitudes of the slopes and intercepts may therefore be somewhat affected. The ϕ parameters measured by Hyland and

Table I
Kinetics of Hydrolysis of *o*-Tolunitrile in Aqueous Perchloric Acid at 133.5°

[$HClO_4$], *M*	$10^5 k_\psi$, sec^{-1} [a]	H_0	$H_0 + \log[H^+]$
1.47	2.12 ± 0.06	−0.59	−0.41
3.01	6.42 ± 0.43	−1.33	−0.86
4.00	12.5 ± 0.55	−1.79	−1.18
4.51	16.0 ± 0.35	−2.02	−1.38
4.99	19.8 ± 0.53	−2.28	−1.58
5.50	32.0[b]	−2.59	−1.85
6.02	38.3 ± 1.15	−2.90	−2.12

[a] Standard deviations are shown. [b] Average of 31.7 ± 0.7 and 32.3 ± 1.4.

Table II
Summary of Rate Correlations

Correlation	Slope	Intercept	σ_y[a]	σ_{sl}[b]	r[c]
($\log k_\psi + H_0$) *vs.* ($H_0 + \log[H^+]$)	+0.61[d]	−4.99	0.03	0.02	0.997
($\log k_\psi + H_0$) *vs.* $\log a_w$	+3.33[e]	*f*	0.04	0.16	0.994
$\log k_\psi$ *vs.* $-H_0$	+0.55	*f*	0.05	0.03	0.994

[a] Standard deviation of points, in the *y* direction, from the linear regression line. [b] Standard deviation of slope. [c] Correlation coefficient. [d] ϕ value. [e] *w* value. [f] Not listed; has no fundamental significance.

O'Connor[3] for benzonitrile hydrolysis diminish from +0.64 at 70° to +0.48 at 111° and crudely extrapolate to about +0.38 at 133.5°. The ϕ parameter we obtain for *o*-tolunitrile hydrolysis at 133.5°, namely +0.61, is considerably higher than +0.38.

From Arrhenius extrapolation of the log k_2^0 values of Hyland and O'Connor to 133.5°, we reckon k_2^0 for benzonitrile hydrolysis at that temperature to be 5.3×10^{-6} M^{-1} sec^{-1}. This compares with 1.1×10^{-5} M^{-1} sec^{-1} for *o*-tolunitrile from our data. The ortho methyl group approximately doubles the hydrolysis rate. This augmentation probably is to be attributed to a favorable effect of *o*-methyl on equilibrium protonation of the nitrile. It also suggests that there is minimal steric hindrance by *o*-methyl to attack of water at carbon of the protonated nitrile.

For hydrolysis of a weakly basic substrate, the ϕ parameter is composite, being the sum of ϕ_e for equilibrium protonation of the substrate and ϕ_r for the step(s) in which the protonated substrate progresses to transition state and thence to products.[5] Inasmuch as only the ϕ_r value could be related to reaction mechanism and there are no data available from which to calculate the ϕ_e value for nitrile protonation, we eschew attempting to draw mechanistic conclusions from our kinetic data.

Experimental Section

A small amount of *o*-tolunitrile was dissolved in a standardized solution of $HClO_4$ in distilled water. Aliquots were sealed in glass ampoules which were immersed, all at once, in a thermostat at 133.5 ± 0.2°. At measured times ampoules were removed, plunged into cold water, and opened, and 2-ml portions transferred by pipet into 10-ml volumetric flasks containing 3 ml of 6 M aqueous NaOH. The flasks were diluted to the mark with distilled water and the absorbances of the resulting solutions were immediately measured at 231 nm by means of a Beckman Model DU spectrophotometer. (Independent measurements showed that in alkaline solution *o*-toluamide and *o*-toluate ion have equal extinction coefficients at 231 nm.) Plots of $\ln (A_t - A_\infty)$ were linear, and the negatives of their slopes (calculated by linear regression analysis) were taken as k_ψ.

Registry No.—*o*-Tolunitrile, 529-19-1; perchloric acid, 7601-90-3.

References and Notes

(1) Research supported in part by the National Science Foundation and the Army Research Office (Durham).
(2) To whom correspondence should be addressed, at the University of California, Santa Cruz, Calif. 95064.
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Nitration of the Acridizinium Ion and Its 6,11-Dihydro Derivative[1]

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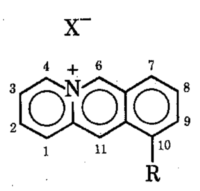
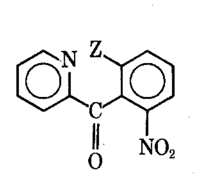
To date, the only clear-cut electrophilic substitution reaction carried out with the unsubstituted acridizinium ion **1** has been sulfonation,[2] which occurs at position 10 of the cation. The mechanism of the halogenation reaction is obscure. It was suggested[3] that at least some of the products were formed by an addition–elimination mechanism. To date, there has been no report of the nitration of the acridizinium ion.



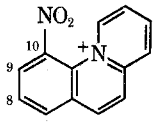
1, R = H
2, R = NO_2



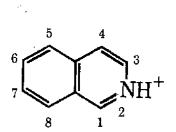
3, Z = COOH
4, Z = H

Earlier experiments showed that, when acridizinium salts are heated with nitric acid, the product is a compound formed by oxidation[4] as well as nitration. When a mixture of concentrated nitric and sulfuric acids at below −5° is used, a mononitro acridizinium salt is obtained in good yield. The product is so susceptible to nucleophilic attack that it can be crystallized satisfactorily only if acid is present. Oxidation of the new nitroacridizinium salt at 100° in concentrated nitric acid afforded a 2-(2-carboxynitrobenzoyl)pyridine which, on decarboxylation, yielded the known[5] 2-(2-nitrobenzoyl)pyridine (**4**). From this, it follows that the acid is **3** and the original nitration product is the 10-nitro derivative (**2**).

The 10 position, like the 8 position, does not bear a positive charge in any of the canonical forms contributing to the resonance hybrid. It is probable that nitration and sulfonation occur predominantly at position 10 (rather than 8) because of the greater reactivity of α positions in polycyclic systems. The observation parallels exactly that of the nitration of the benzo[*c*]quinolizinium ion[6] (yielding **5**) in that the nitration occurs in the ring most remote from the positive charge and at that α position which does not bear a positive charge in any of the canonical forms contributing to the resonance hybrid. Another interesting parallel is the nitration of isoquinoline. In mixed acid, in which it exists as its conjugate acid **6**, it affords the 5-nitro derivative in 90% yield.[7] This orientation is explicable on the same basis as that of the two benzoquinolizinium systems (**2** and **5**). Reduction of the nitro group of **2** is accompanied by reduction of the quinolizinium system.

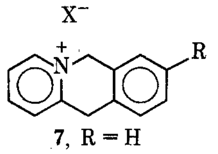


5



6

As was reported earlier,[8] acridizinium salts can be reduced over a palladium catalyst to yield the 6,11-dihydro product (**7**). Nitration of **7** afforded a 70% yield of 8-nitro-6,11-dihydroacridizinium salt (**8**), the identity of which was established by oxidation to the known[4] 2-(2-carboxy-4-nitrobenzoyl)pyridine (**10**). The discovery that this oxidation could be carried out by the use of permanganate prompted a reinvestigation of the oxidation of acridizinium bromide. In the first paper[9] dealing with acridizinium salts, the statement was made that the crude permanganate oxidation product, obtained in 81% yield, was impure phthalic acid. This statement, based only on a



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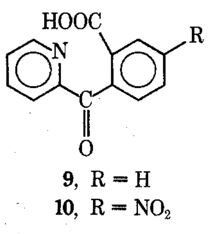
8, R = NO_2



9, R = H
10, R = NO_2