the thermodynamic data reported above. The ratio of K_A to K_B is indeed independent of temperature ($\Delta H°_A = \Delta H°_B$) as predicted by the relationship $K_B/K_A = k_1/k_{-1}$ and the diffusion controlled nature of both k_1 and k_{-1}.

The rate of attainment of the stationary state is also consistent with the mechanism. Excellent linear plots of the relationship

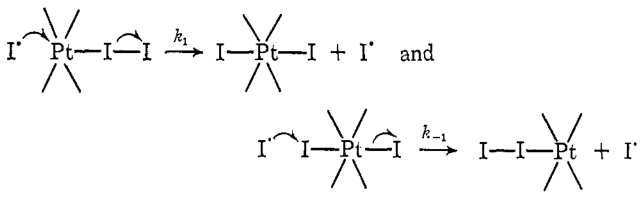
$$\ln\left(\frac{A_0 - A_e}{A_t - A_e}\right) = k_{\text{obsd}}\int_0^t\left(\frac{e^{mt} - 1}{e^{mt} + 1}\right)dt$$

(where A is absorbance and $m = 4(\varphi I_a k_2)^{1/2}$) were obtained. These data also predict that the reaction should exhibit a pronounced photo after effect. This was investigated by monitoring a reaction solution with a very low-beam flux subsequent to its irradiation with a light pulse of much greater flux. Very large photo aftereffects were observed. In some cases the reaction went to equilibrium before the iodine atom concentration had decayed to a steady concentration. These data give $k_1 = 1.7 \times 10^9$ l. mol^{-1} sec^{-1} at $-0.9°$ in good agreement with the stationary-state values.

The effect of radical initiators and inhibitors was investigated. Addition of O_2, DPPH, hydroquinone, and allyl iodide had negligible effects on the rates. This insensitivity to chemical additives probably results from the rapidity of the rates of reaction of iodine atoms with A and B.

The kinetics of the reaction in cyclohexane are very similar to those of the reaction in CCl_4 and give $k_1 \simeq 1 \times 10^9$ l. mol^{-1} sec^{-1} at 20.6°. On the other hand the cyclohexane system exhibits a thermal pathway (k''), $k_{\text{obsd}} = k'' + k'I_a^{1/2}$, and its mechanism is currently being investigated.

Previous studies[11] of the structures of 1:1 halogen complexes with n donor atom (N, O, S, and Se) Lewis bases indicate that the most probable structure of A would contain a linear Pt–I–I arrangement which coincides with the principal axis of the planar $Pt^{II}(acac)_2$ moiety. An empty σ^* orbital on the iodine molecule is of correct symmetry to accept electron density from the d_{z^2} orbital of the platinum atom.[12] The very rapid reversible propagation step is consistent with this structure in that facile iodine atom attack can occur along the principal axis of either A or B.



It is of interest that the adduct $Pt^{II}(CN)_4(Br_2)^{2-}$ has been postulated[13] as a transient intermediate in the oxidative addition reaction: $Pt(CN)_4^{2-} + Br_2 \rightleftarrows$ *trans*-$Pt(CN)_4Br_2^{2-}$. Adducts formed between Lewis acids and coordinatively unsaturated basic metal complexes may be of considerable mechanistic importance in oxidative addition reactions.

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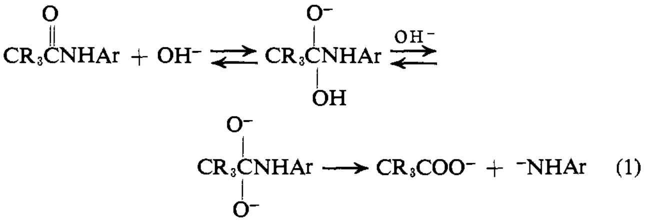
(14) Department of Chemistry, Imperial College of Science and Technology, London, SW7 2AY, United Kingdom.

D. Hopgood,*[14] R. A. Jenkins
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706 and
The Inorganic Chemistry Research Laboratories
Imperial College of Science and Technology
London, SW7 2AY, United Kingdom
Received January 27, 1973

Specific Base–General Acid Catalysis of the Alkaline Hydrolysis of *p*-Nitrotrifluoroacetanilide

Sir:

The mechanism of the alkaline hydrolysis of anilides with strongly electron-withdrawing ring substituents has been a subject of considerable interest lately.[1-4] It was originally proposed that these anilides hydrolyze by a pathway involving expulsion of a negatively charged anilide ion from a dianion intermediate without the aid of a general acid catalyst (eq 1).[1] This



$$\mathrm{CR_3\overset{\overset{O}{\|}}{C}NHAr + OH^- \rightleftarrows CR_3\overset{\overset{O^-}{|}}{\underset{\underset{OH}{|}}{C}}NHAr \overset{OH^-}{\rightleftarrows} CR_3\overset{\overset{O^-}{|}}{\underset{\underset{O^-}{|}}{C}}NHAr \longrightarrow CR_3COO^- + {}^-NHAr} \qquad (1)$$

interpretation was based on work with *p*-nitroacetanilide and *p*-formylacetanilide, which are not hydrolyzed at convenient rates in moderately basic solution, so that the possibility of general catalysis was not examined directly. Recently, Menger and Donohue[4] have found that the alkaline hydrolysis of *N*-acetylpyrrole shows similar kinetic behavior to *p*-nitroacetanilide and *p*-formylacetanilide. Since *N*-acetylpyrrole reacts considerably faster than acetanilides they were able to search for general catalysis. The finding of no observable general catalysis of this reaction confirms the previously proposed mechanism for ring-activated anilides.[1]

We have now examined the alkaline hydrolysis of the highly reactive *p*-nitrotrifluoroacetanilide and find that, contrary to expectations, this reaction *does* show kinetic general base catalysis. We interpret this result to mean that there are two pathways for cleavage of the tetrahedral intermediate. In addition to cleavage of the dianion to give *p*-nitroanilide ion and trifluoroacetate ion without general catalysis, a second mode of breakdown exists which involves cleavage of the monoanion *with* general acid catalysis to give *p*-nitroaniline and trifluoroacetic acid directly. These two pathways involve loss of the negative *p*-nitroanilide ion from the dianion intermediate but loss of neutral *p*-nitroaniline

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(1) R. M. Pollack and M. L. Bender, *J. Amer. Chem. Soc.*, **92**, 7190 (1970).

(2) R. H. DeWolfe and R. C. Newcomb, *J. Org. Chem.*, **36**, 3870 (1971).

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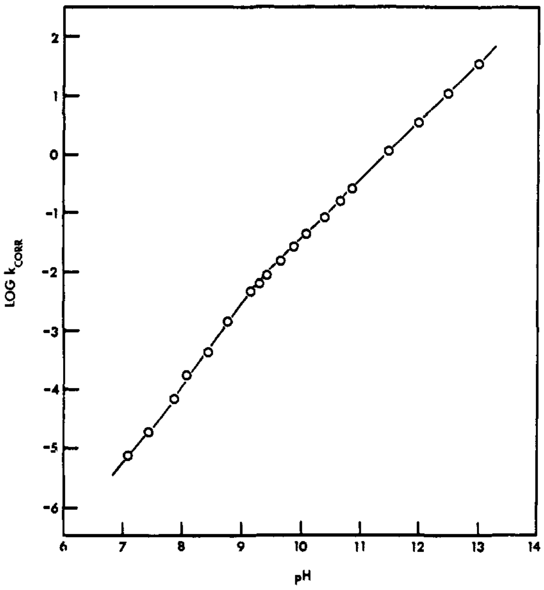
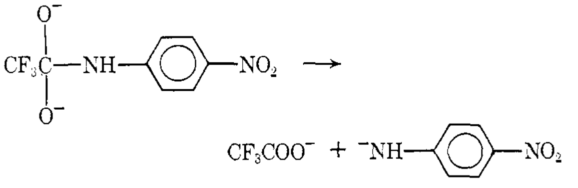
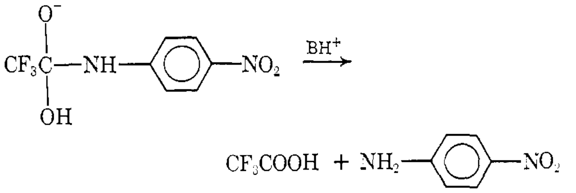


Figure 1. Plot of the rate constant for alkaline hydrolysis of *p*-nitrotrifluoroacetanilide (corrected for ionization of substrate) *vs.* pH. The line is calculated from eq I.

from the monoanion. Although these two intermediates differ by only one proton, their mode of breakdown is surprisingly different.

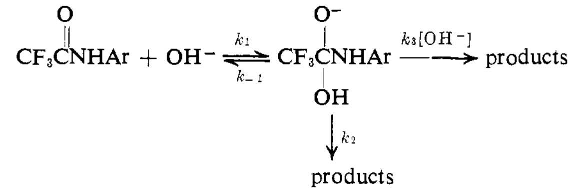


(2a)



(2b)

Although the hydrolysis rate of *p*-nitrotrifluoroacetanilide is complicated by ionization of the amide nitrogen to give an anion which is generally assumed to be unreactive,[1,2,5,6] this side reaction can be easily corrected for. We measured the p*K* of trifluoroacetanilide (8.2 ± 0.1) and all rate constants reported here have been corrected for this ionization. The hydroxide ion catalyzed rate constants corrected for substrate ionization are shown in Figure 1.[7] The pH-rate profile may be analyzed according to eq 3. Application of the steady-state assumption gives



$$\mathrm{CF_3\overset{\overset{O}{\|}}{C}NHAr} + \mathrm{OH^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CF_3\overset{O^-}{\underset{OH}{C}}NHAr} \xrightarrow{k_3[\mathrm{OH^-}]} \text{products} \quad \downarrow k_2 \ \text{products} \tag{3}$$

$$k_{\text{corr}} = \frac{k_1(k_2 + k_3[\mathrm{OH^-}])[\mathrm{OH^-}]}{k_{-1} + k_2 + k_3[\mathrm{OH^-}]} \tag{I}$$

Evaluation of these parameters gives $k_1 = 3.6 \times 10^2$ $M^{-1}\,\text{sec}^{-1}$, $k_1/k_2 = 8$, and $k_3/k_2 = 3 \times 10^6\,M^{-1}$.

At pH values greater than 9 the reaction is first order in hydroxide ion with no detectable catalysis by buffer (bicarbonate-carbonate). The change in slope from greater than one to one indicates that at high pH, the addition of hydroxide ion (k_1) has become rate determining.[1,8] The value of k_1, obtained from this portion of the curve, is about 20 times faster than the corresponding value for trifluoroacetanilide itself.[5,6] A slightly enhanced rate for addition of hydroxide ion is to be expected for *p*-nitrotrifluoroacetanilide due to the presence of the highly electron-withdrawing nitro group.[5,9,10]

At lower pH's (7.2–8.7) the rate falls off more steeply with decreasing pH, indicating that breakdown of the intermediate has become rate determining. In addition, there is significant catalysis by tris(hydroxymethyl)aminomethane (Tris) buffers. The buffer-catalyzed rate is proportional to the concentration of free base and shows no variation with hydroxide ion concentration (Table I). We interpret this result to mean that there is general acid catalysis of the breakdown of the monoanion (k_2) but not of the dianion (k_3). General acid catalysis of k_3 should lead to a term in [OH⁻][Tris],[11] whereas general acid catalysis of the k_2 step should lead to a term depending solely on the concentration of free Tris, as is observed. Although breakdown of the monoanion requires a general acid, breakdown of the dianion does not (eq 2).

Table I. Rate Constants for Tris Catalyzed Hydrolysis of *p*-Nitrotrifluoroacetanilide

pH	$[\text{Tris}]_{\text{free}}$	k, M^{-1} sec$^{-1\,a}$	k_{corr}, M^{-1} sec$^{-1\,a,b}$
7.21	0.004–0.020	$2.06 \pm 0.06 \times 10^{-3}$	$2.32 \pm 0.13 \times 10^{-3}$
7.49	0.008–0.040	$2.02 \pm 0.10 \times 10^{-3}$	$2.53 \pm 0.16 \times 10^{-3}$
7.91	0.018–0.090	$1.60 \pm 0.05 \times 10^{-3}$	$2.50 \pm 0.19 \times 10^{-3}$
8.06	0.028–0.140	$1.30 \pm 0.03 \times 10^{-3}$	$2.53 \pm 0.29 \times 10^{-3}$
8.47	0.056–0.280	$9.6 \pm 0.5 \times 10^{-4}$	$2.63 \pm 0.49 \times 10^{-3}$
8.74	0.108–0.540	$6.0 \pm 0.2 \times 10^{-4}$	$2.86 \pm 0.71 \times 10^{-3}$

[a] Rate constants were obtained by weighted least-squares analysis of plots of k^{obsd} *vs.* $[\text{Tris}]_{\text{free}}$. Errors are standard deviations of these plots. [b] Corrections are bases on spectral determinations of per cent *p*-nitrotrifluoroacetanilide ionized in the buffers used.

Further evidence for this interpretation may be obtained by considering the substituent effect on each of the two processes. The overall rate constant for cleavage of the dianion is about 10^4 greater for *p*-nitrotrifluoroacetanilide than would be expected on the basis of other ring-substituted trifluoroacetanilides.[5] This result is consistent with the generation of a negative charge on the amide nitrogen in the transition state.

The k_2 process, on the other hand, shows only a slight

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(5) C. E. Stauffer, *J. Amer. Chem. Soc.*, **94**, 7887 (1972).

(6) S. O. Eriksson and C. Holst, *Acta Chem. Scand.*, 20, 1892 (1966).

(7) The reaction rate was measured spectrophotometrically at 400 nm at 25.0° (μ 0.2). Hydroxide ion rates were obtained by extrapolation to zero buffer concentration or were measured directly in NaOH (pH >11). Rate constants were corrected for ionization of the substrate by dividing the observed rate constant by the per cent substrate un-ionized at that pH.

(8) R. L. Schowen, H. Jayaraman, and L. Kershner, *J. Amer. Chem. Soc.*, 88, 3373 (1966).

(9) L. D. Kershner and R. L. Schowen, *J. Amer. Chem. Soc.*, **93**, 2014 (1971).

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rate enhancement for *p*-nitrotrifluoroacetanilide over other ring-substituted trifluoroacetanilides. The hydroxide ion catalyzed rate constant is about 10 times faster for *p*-nitrotrifluoroacetanilide and the Tris catalyzed rate constant is virtually identical with that for trifluoroacetanilide itself.[5,12] The small variation of these rate constants with substituent shows that little or no negative charge is formed on the amide nitrogen at the transition state, even for *p*-nitrotrifluoroacetanilide, and is consistent with the leaving group being the free nitroaniline molecule rather than a negative anilide ion. In addition, the observation of general catalysis for this pathway demands that the base be present in the activated complex, although several functions can be envisioned for the base molecule.[11]

We find the difference in mode of breakdown of these two intermediates surprising, especially in view of the fact that for other anilides the monoanion and the dianion have been found to decompose by the same mechanism.[9] Even when a change in mechanism with substituent is postulated, it appears that the change occurs at the same place for both the monoanion and the dianion.[9]

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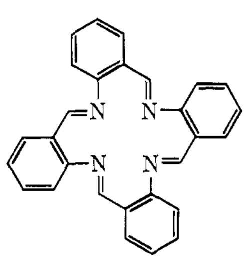
R. M. Pollack,* T. C. Dumsha
Department of Chemistry
University of Maryland Baltimore County
Baltimore, Maryland 21228

Received March 12, 1973

Alkoxyethylidene Functions as Reactive Sites for the Attachment of Pendent Groups to Complexes of Macrocyclic Ligands. Crystal Structure and Reactivity Patterns

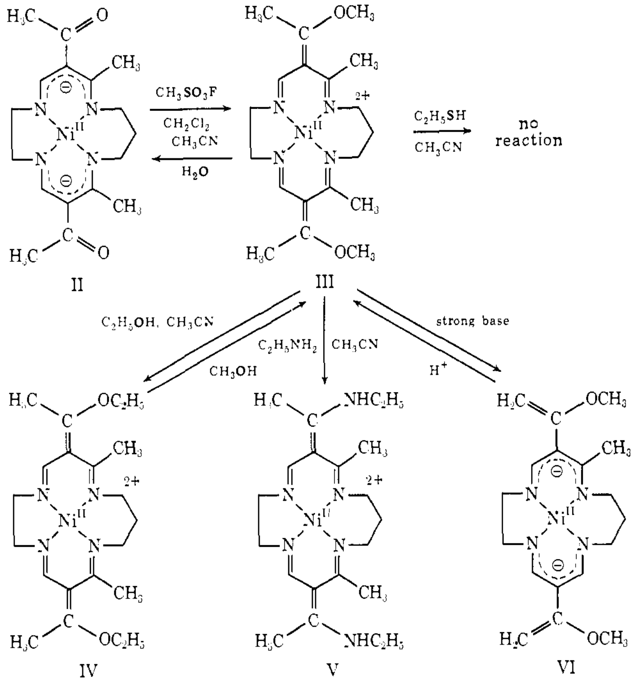
Sir:

Among the major synthetic goals related to the use of macrocyclic transition metal complexes as models for biological systems is activation of the planar chelate rings toward attachment of other functional groups properly oriented to allow interaction with the central metal ion *via* its axial coordination sites. Synthetic macrocyclic complexes having such pendent functional groups could then be used to examine the chemistry associated with these features in naturally occurring systems. One possible route to this type of system has been reported involving the reversible addition of a variety of nucleophiles to the azomethine carbon atoms in Ni(II) and Cu(II) complexes of the macrocycle I.[1-3]



I

Scheme I



We wish to report the results of our studies on the alkylation of the carbonyl groups of II[4-6] (Scheme I) leading to the formation of III. Treatment of II with methyl fluorosulfonate in dichloromethane produced III, originally formulated as the product of N-alkylation.[6] The X-ray crystal structure, however, establishes the site of alkylation to be as shown in III, and the methoxyethylidene groups display an interesting selectivity in their reactions with nucleophiles, providing a convenient route for the attachment of side chains to the ligand framework.

6,14-Bis(1-methoxyethylidene)-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,7,12,15-tetraenenickel(II) perchlorate, $C_{12}H_{30}N_4O_{10}NiCl_2$ (III):[7] yellow rods from acetone; orthorhombic; *Pbcm*; $a = 8.257$ (4), $b = 13.94$ (1), $c = 22.11$ (1) Å; $M = 604.09$; $D_{\text{measd}} = 1.574$ g/cm³, $Z = 4$, $D_{\text{calcd}} = 1.577$ g/cm³; μ (Mo Kα) 10.3 cm^{-1}. $R = 0.046$ for 2228 independent reflections above background for a structure with molecular parameters shown in Figure 1. The molecule lies astride a crystallographic mirror plane. The bond lengths and angles are consistent with a bonding scheme involving localized double bonds. Remarkably, the central six-membered ring exists in the *boat* form, the Ni and C segments being tilted up 35 and 56°, respectively, from the central four atom plane defined

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(1) L. T. Taylor, F. L. Urbach, and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 1072 (1969).

(2) V. Katović, L. T. Taylor, and D. H. Busch, *ibid.*, **91**, 2172 (1969).

(3) V. Katović, L. T. Taylor, and D. H. Busch, *Inorg. Chem.*, **10**, 4581 (1971).

(4) 6,14-Diacetyl-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,-12,14-tetraenatonickel(II) (II) was prepared by the method of Jäger.[5] Satisfactory elemental analyses were obtained for all complexes reported.

(5) E. Jäger, *Z. Chem.*, **8**, 392 (1968).

(6) C. J. Hipp and D. H. Busch, *J. Chem. Soc., Chem. Commun.*, 737 (1972).

(7) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-4465. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.