

Table I. Coupling Constants and *E/Z* Diastereomer Ratios in the Nmr Spectra of the Imidates 1a-d and 2^a

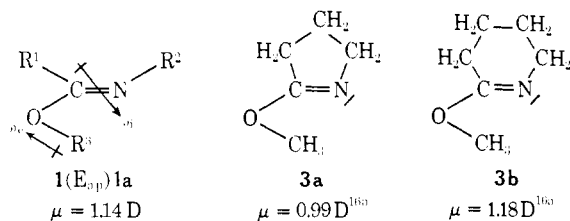
Compd	Solvent	⁵ J _{trans} , Hz ^b	⁵ J _{cis} , Hz ^b	<i>E:Z</i>
1a	CCl ₄		0.4 q	100:0
	CD ₃ OD, ^c CH ₃ OH	1.2 q	0.4 q	95:5
1b	CCl ₄		0.3 (R ¹ t)	100:0
	CD ₃ OD	1.0 (R ¹ t)	0.3 (R ¹ t)	95:5
1c	CCl ₄	1.3 q	0.5 q	69:31
	CD ₃ OD	1.3 q	0.5 q	56:44
1d ^d	CCl ₄			87:13
	CD ₃ OD			71:29
2	CCl ₄	1.4 (CH ₃ t)		

^a All spectra were recorded on a Varian A-60 and HA-100 nmr spectrometer at +36° unless otherwise noted. The internal standard was TMS, the concentration was 0.1–0.5 mol/l. ^b The "trans" homoallylic coupling constant belongs to the signals R¹ and R² of the *Z* diastereomer of 1, ⁵J_{cis} coupling occurs in 1 (*E*); determined from spectra taken at a sweep width of 50 Hz. ^c We found that slow exchange of CH₃O with CD₃O takes place in CD₃OD solutions of 1a at room temperature. Furthermore, after some days the spectra show a decrease of R¹ signal intensity and an increase of CH₃OH. When methanol was used as a solvent, no spectral changes were observed. Obviously slow imine-enamine tautomerism had occurred with predominating imine concentration. Similar effects have been described before in the cyclic *O*-ethylvalerolactams: V. G. Granik, B. M. Pyatin, J. V. Persianova, E. M. Peregleni, N. P. Kostyuchenko, R. G. Glushkov, and Y. N. Sheinker, *Tetrahedron*, **26**, 4367 (1970). ^d Measured at -14°.

C-CH₃ (0.16 ppm), N-CH₃ (0.23 ppm), O-CH₃ (0.45 ppm)).

This shift pattern indicates that 1a exists in the *E* form, since complexation takes place on nitrogen rather than on the ether oxygen due to the more basic character of the imine nitrogen in intramolecular competition.¹⁴

The preference for the *E* configuration may be attributed to the conformation at the R³-O bond in imidates.^{15,16} The lowest dipole moments found for imino esters (1, R² = H, R³ = C₂H₅)¹⁵ and for various *N*-alkyl imidates¹⁶ favor a (*E*_{ap}) (antiperiplanar)¹⁷ form. In fact the dipole moment measurement of 1a turned out to be an appropriate independent method in support of the configurational assignment taken from the nmr spectra. For the acetimidate, 1a, we measured a dipole moment of $\mu = 1.14 (\pm 0.08)$ D¹⁸ at 20° in carbon tetrachloride (calcd $\mu = 1.04$ D), which is in good agreement with the values obtained for imidates, e.g., 3a and 3b,^{16a} having the same configuration at



(14) (a) H. Hart and G. M. Love, *Tetrahedron Lett.*, 625 (1971); (b) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971).

(15) H. Lumbroso, D. M. Bertin, and P. Reynaud, *C. R. Acad. Sci.*, 261, 399 (1965); H. Lumbroso and P. J. W. Schuijl, *C. R. Acad. Sci., Ser. C*, 264, 925 (1967); H. Lumbroso and D. M. Bertin, *Bull. Soc. Chim. Fr.*, 1728 (1970).

(16) (a) O. Exner and O. Schindler, *Helv. Chim. Acta*, **55**, 1921 (1972). (b) H. Lumbroso, and G. Pappalardo, personal communication.

(17) Using the nomenclature of analogous carbonic acid esters: W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960).

(18) Measurement on a dipolmeter DM 01, WTW, Weilheim/Germany; cell DR L2, frequency 2 MHz.

the C=N bond and a similar conformation at the O-R³ bond.

The amount of diastereomer (*Z*_{sp}) with the higher dipole moment (calcd $\mu = 2.40$ D) can increase when the partial compensation of the group dipole moment μ_i (-O-C=N-C) is diminished by the bond dipole moment μ_e (R³-O). This is the case when the imidate is dissolved in the protic solvent methanol (1a-d) or if R³ is a bulky substituent with a more electronegative carbon atom (1c). For steric reasons the *E* configuration is less favored in 1d than in 1a or 1b (Table I). Similar effects have recently been observed in thioimides.⁸

In contrast to the above mentioned publication,¹ we measured barriers to inversion on nitrogen of $\Delta G^\ddagger < 23$ kcal mol⁻¹ as predicted for this type of imine derivatives.¹⁹ Using the relationship $k_c = \pi \cdot \Delta\nu / \sqrt{2}$ and the Eyring equation²⁰ we obtained a free enthalpy of activation $\Delta G_c^\ddagger = 19.8$ kcal mol⁻¹ for 1c ($\Delta\nu_{C-CH_3} = 17$ Hz, coalescence temperature $T_c = +110^\circ$, solvent *o*-dichlorobenzene) and $\Delta G_c^\ddagger = 15.9$ kcal mol⁻¹ for 1d ($\Delta\nu_{O-CH_3} = 18.5$ Hz, $T_c = +37.5^\circ$, solvent CCl₄). The lower value of 1d results from steric interactions in the favored ground state (*E*) and is in accordance with the data derived from thioimides.⁸

The governing factors determining the *E/Z* diastereomer ratios of imidates 1a-d are dipole interactions and steric influences. Contrary to the results of Moriarty, *et al.*,¹ no hints of interorbital effects in imidates could be detected.

(19) H. Kessler, personal communication.

(20) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., 1965, Chapter 9.

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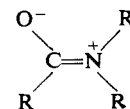
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Electronic and Steric Effects of Substitution at Nitrogen on Hindered Rotation in Formanilides

Sir:

In contrast to the well-documented effects of nitrogen substituents on the inversion process in amines,^{1,2} the electronic and steric effects of substitution at nitrogen on the rotational barrier in amides have received little systematic attention.^{2,3} An increase in electron density at the amide nitrogen should theoretically result in an increase in the activation energy because of an increase in the contribution of the resonance structure



and the resulting stabilization of the ground state. An increase in size of the substituent at nitrogen should result in greater destabilization of the ground state than that of the transition state and consequently a decrease in activation energy. The *N*-alkylformanilide molecule is an ideal system in which to test these expectations;

(1) J. B. Lambert, *Top. Stereochem.*, **6**, 19 (1971).

(2) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).

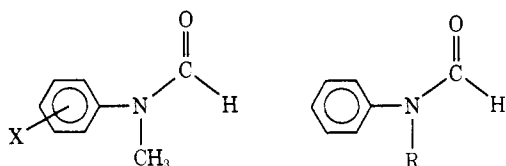
(3) W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, **70**, 517 (1970).

Table I. Rotational Parameters for Formanilides

X	<i>T</i> _c , °K	Δ <i>ν</i> , Hz	$P_b \pm 0.02$		$\Delta G^\ddagger (\pm 0.3 \text{ kcal/mol})$	
			<i>P</i> _b , <i>T</i> _c	<i>P</i> _b , 0°	Δ <i>G</i> _a [‡] ^a	Δ <i>G</i> _b [‡] [‡]
			XC ₆ H ₄ N(CH ₃)CHO ^b			
<i>p</i> -NO ₂	I	309.4	13.2	0.16	17.1	16.1
<i>p</i> -Cl	II	326.0	14.1	0.09	18.4	16.9
<i>m</i> -OCH ₃	III	325.3	9.8	0.07	18.8	17.1
<i>p</i> -H	IV	328.7	13.8	0.08	18.7	17.1
<i>p</i> -CH ₃	V	335.9	13.7	0.10	18.9	17.5
<i>p</i> -OCH ₃	VI	341.6	12.5	0.15	19.0	17.8
<i>p</i> -N(CH ₃) ₂	VII	348.1	10.1	0.06	20.3	18.3
			C ₆ H ₅ NXCHO ^c			
C ₂ H ₅	VIII	337.3	23.8	0.17	18.3	17.2
CH(CH ₃) ₂	IX	327.3	6.4	0.18	18.5	17.5
C(CH ₃) ₃	X	341.8	16.3	0.26	18.4	17.7

^a Δ*G*_a[‡] = Δ*G*[‡] for conversion of major isomer, a, to minor isomer, b. ^b 5% in ClC₆H₅, except III and VII which were 30% in ClC₆H₅. ^c 30% in C₆H₆.

the electron density at the nitrogen can be varied without change in steric hindrance by meta and para ring substitution, while the steric effect can be altered by change of the *N*-alkyl substituent. We have, therefore, prepared a series of substituted *N*-methylformanilides and



a series of *N*-alkylformanilides and have examined their nmr spectra as a function of temperature.

The low temperature spectra of each of the *N*-methyl derivatives in chlorobenzene contain a doublet (*J* = 0.4–0.6 Hz) and a much less intense singlet (area ratio *ca.* 15:1) in the *N*-methyl region and two singlets (unresolved quartets with half height width of 2 Hz, area ratio *ca.* 15:1) in the formyl region. The resonances within each region coalesce as the temperature is increased and can be attributed therefore to the rotational isomers. The rotamer assignments for *N*-methylformanilide have been discussed previously.⁴

The nmr spectra of *N*-ethyl-, *N*-isopropyl-, and *N*-*tert*-butylformanilide also contain resonances attributable to rotational isomers (*e.g.*, two sets of triplets and quartets for the *N*-ethyl group of the ethyl derivative). Table I contains the relative populations of the minor isomers at 0° and at the coalescence temperature. At 0° the data indicate an increase in abundance of the minor isomer as the size of the alkyl group is increased. Primarily because of the considerable errors inherent in the determination of small populations and the magnification of error which occurs upon extrapolation, the populations at the coalescence temperature show a less definite trend. Dilution of each compound with benzene results in a greater upfield shift for the minor isomer which therefore most likely has the alkyl group trans to the carbonyl group.³ The most abundant isomer consequently contains the alkyl group *cis* to carbonyl, in agreement with previous observations on *N*-methyl- and *N*-ethylformanilides.⁴ The increase in the population of the least abundant isomer as the size of the alkyl group increases is also in agreement with isomer ratio–size correlations in formamides.³

(4) A. J. R. Bourn, D. G. Gillies, and E. W. Randall, *Tetrahedron*, **22**, 1825 (1966).

The free energies of activation for the rotational process in the compounds of both series were calculated from the *N*-alkyl resonances by the method of Shanan-Atidi and Bar-Eli.⁵ This method has been shown to give Δ*G*[‡] values in good agreement with those obtained from total line shape analysis.⁶ The chemical shift difference (Δ*ν*) at the coalescence temperature (*T*_c) was obtained by extrapolation of a least-squares plot of Δ*ν* *vs.* *T* prepared from data for four or five temperatures in the slow rotation region. The populations (*P*_a, *P*_b) at *T*_c were obtained similarly from least-square plots of log *P*_a/*P*_b *vs.* 1/*T*. The free energy of activation as well as *T*_c, Δ*ν*, and *P*_b (population of the least abundant isomer) at the coalescence temperature and *P*_b at 0° for each compound are listed in Table I. The free energy of activation for compound IV calculated from spectra obtained by decoupling the *N*-methyl resonances was within experimental error of the value reported in the table. The dependence of Δ*G*[‡] on concentration was also tested for several compounds and was found to be negligible. Since the rotational isomers were not observed in nonaromatic solvents (CCl₄, CHCl₃, CH₂Cl₂, CH₃NO₂, and CH₃CN were investigated), the effect of solvent could not be explored.

As is apparent from Table I, the free energies of activation for the *N*-methylformanilides show a definite relation to the electronic effect of the ring substituent. Indeed, the least-squares correlation coefficient for a plot of Δ*G*[‡] *vs.* the Hammett *σ* constant of the substituent (slope (Δ*G*_b[‡]) = –1.4, intercept (Δ*G*_b[‡]) = 17.2, correlation coefficient (Δ*G*_b[‡]) = 0.985; slope (Δ*G*_a[‡]) = –1.9, intercept (Δ*G*_a[‡]) = 18.7, correlation coefficient (Δ*G*_a[‡]) = 0.985) is good. Since the entropies of activation for the rotation about the carbonyl–nitrogen bond in these structurally similar derivatives are probably similar, the activation energy should parallel Δ*G*[‡]. Thus, the activation energy and free energy can be related directly to the electron density at the nitrogen, in agreement with the theoretical prediction. The effect of aromatic substituents on Δ*G*[‡] is presumably the result of destabilization of the ground state by electron-withdrawing groups and stabilization of the transition state by resonance interaction of nitrogen with *π*-withdrawing groups. The recently reported low free

(5) H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, **74**, 961 (1970).

(6) D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).

energy of activation for *N*-fluoro-*N*-methylformamide is in harmony with this conclusion.⁷

The dependence of the rotational barrier on the nature of the aromatic substituent can be contrasted with the analogous relationship for the inversion process in amines. Electron-releasing substituents also increase the barrier to inversion in arylaziridines, but ΔG^\ddagger is more strongly influenced by the substituent (slope (ΔG^\ddagger vs. σ^-) = -2.8 at -60°).⁸

The data of Table I also reveal that the values of ΔG^\ddagger do not vary significantly with the size of the *N*-alkyl group. The same result has been reported for *N,N*-dialkylformamides.⁹ Therefore, if the activation energies do parallel the free energies of activation and if an increase in size of the alkyl group does indeed result in a greater destabilization of the ground state, this barrier-lowering steric effect must be compensated for by a barrier-increasing electronic effect.

Acknowledgment. The authors are indebted to the Camille and Henry Dreyfus Foundation for partial support of this work.

(7) J. Cantacuzene, J. Leroy, R. Jantzen, and F. Dudragne, *J. Amer. Chem. Soc.*, **94**, 7924 (1972).

(8) J. D. Andose, J.-M. Lehn, K. Mislow, and J. Wagner, *J. Amer. Chem. Soc.*, **92**, 4050 (1970).

(9) T. H. Siddall, III, W. E. Stewart, and F. D. Knight, *J. Phys. Chem.*, **74**, 3580 (1970).

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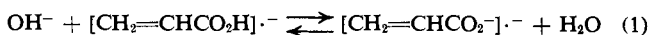
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A Proposed Mechanism for the Base Catalyzed Protonation of the e_{aq}^- Adduct to Acrylate

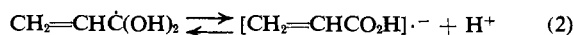
Sir:

A recent letter¹ has reported data on the e_{aq}^- adduct to acrylate which the authors interpret as showing a *base catalyzed protonation* on carbon of the dianion radical to give the radical $\text{CH}_3\dot{\text{C}}\text{HCO}_2^-$. No mechanism for this unusual catalysis was proposed. In the course of esr studies of the anion radicals derived from the reaction of e_{aq}^- with fumarate, it was found² that the fully dissociated form $[-\text{O}_2\text{CCH}=\text{CHCO}_2^-]^-$ reacted slowly with water (millisecond time scale) to give a radical protonated on carbon ($-\text{O}_2\text{CCH}_2\dot{\text{C}}\text{HCO}_2^-$) while the form $[-\text{O}_2\text{CCH}=\text{CHCO}_2\text{H}]^-$ reacted at a significantly slower rate. A greater reactivity of the more highly charged species should carry over to the acrylate system, and consequently we would like to suggest an alternative interpretation of that data¹ as well as a mechanism for the base catalysis.

We propose that the equilibrium for the second dissociation



corresponds to a pK_a of above 11 and that the value of 7.0 determined for this system corresponds to the first dissociation



(1) E. Hayon, N. N. Lichtin, and V. Madhavan, *J. Amer. Chem. Soc.*, **95**, 4762 (1973).

(2) O. P. Chawla and R. W. Fessenden, *J. Phys. Chem.*, to be submitted for publication.

rather than the second as stated.¹ The immediate appearance of $\text{CH}_3\dot{\text{C}}\text{HCO}_2^-$ at pH 12 ($k > 7 \times 10^6 \text{ sec}^{-1}$)³ means that, in this scheme, the dianion radical $[\text{CH}_2=\text{CHCO}_2^-]^-$ must protonate on carbon at this rate. The rate at lower pH values is reduced because of the shift of equilibrium 1 to the left and the fact that the form $[\text{CH}_2=\text{CHCO}_2\text{H}]^-$ protonates on carbon more slowly ($k = 7.7 \times 10^4 \text{ sec}^{-1}$).¹ It is the protonation of this latter form which is catalyzed by OH^- by a shift of equilibrium 1.

The state of dissociation of the e_{aq}^- adduct to acrylate can readily be checked by pulse conductivity measurements as was done for the adducts to fumarate and maleate.⁴ If the e_{aq}^- adduct remains fully dissociated at pH 8–11 as originally suggested,¹ then the net conductivity change will involve conversion of $\text{CH}_2=\text{CHCO}_2^-$ to $[\text{CH}_2=\text{CHCO}_2^-]^-$ and the removal of a corresponding amount of OH^- by the H^+ produced by the pulse.⁵ Because the equivalent conductance of OH^- (192)⁶ is considerably higher than that associated with organic ions (40–70), a decrease in equivalent conductance (per equivalent of e_{aq}^- produced) of 120–150 units will occur. If the radical reacts with water to give a protonated form (either $[\text{CH}_2=\text{CHCO}_2\text{H}]^-$ or $\text{CH}_3\dot{\text{C}}\text{HCO}_2^-$) then the OH^- is regenerated and the conductance will return to a value near that before the irradiation.

An ac conductivity method is necessary because the starting material is an electrolyte. Experiments were carried out using the 10-MHz conductivity apparatus previously described,⁴ and the transient signal on the oscilloscope was photographed.⁷ Radiolysis was with 2.8 MeV electrons and the dose was monitored with a secondary emission chamber. Sensitivity of the conductivity detector was calibrated by use of a slightly acid (pH ~ 5) solution of saturated CH_3Cl containing 0.1 *M* *tert*-butyl alcohol.⁸ The initial experiment used 0.5×10^{-3} *M* acrylic acid (Eastman Chemical Co.) neutralized to pH 9.3 with KOH and containing 0.1 *M* *tert*-butyl alcohol to scavenge OH. An experimental trace with this solution is shown in Figure 1a. The initial decrease in conductance (3 mm) measured at 3 μsec after the pulse⁹ corresponds to a value of about 15–20 units with no fast decay evident. This value is much less than that expected if the e_{aq}^- adduct were to exist as $[\text{CH}=\text{CHCO}_2^-]^-$. The data presented by Hayon, *et al.*,¹ for the rate of protonation on carbon give a first-order rate

(3) Based on the stated time resolution of 0.1 μsec , the half-life for protonation to form $\text{CH}_3\dot{\text{C}}\text{HCO}_2^-$ must be $>0.1 \mu\text{sec}$ for a first-order rate of $>7 \times 10^6 \text{ sec}^{-1}$.

(4) J. Lillie and R. W. Fessenden, *J. Phys. Chem.*, **77**, 674 (1973).

(5) Reaction of OH with *tert*-butyl alcohol does not produce any conducting species and therefore only the fate of e_{aq}^- and H^+ must be considered.

(6) Values of equivalent conductance given here are in units of $\Omega^{-1} \text{ cm equiv}^{-1}$ and pertain to 25° as given in "Handbook of Chemistry and Physics," 45th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1966, p D89.

(7) Previously the transient signal was digitized at a number of times, and the data were processed by computer. This approach has been abandoned temporarily because of equipment changes and the need to rewrite the program.

(8) For this solution, the conductivity change corresponds to production of $\text{H}^+ + \text{Cl}^-$ with an equivalent conductance of 426. The e_{aq}^- yield for a saturated CH_3Cl solution was taken as 3.12 as a result of corrections for spur scavenging. Other yields were also corrected for this effect: T. I. Balkas, J. H. Fendler, and R. H. Schuler, *J. Phys. Chem.*, **74**, 4497 (1970).

(9) Currently, the conductivity detection is gated off during the pulse, and for about 2 μsec after, to prevent recovery problems. The output of the detector becomes valid at about 3–3.5 μsec after the end of the pulse.