reaction paths of these ions are normally those which lead to aromatization by elimination of a cation, usually a proton. However, certain structural features or reaction conditions can permit other carbonium ion processes to become competitive with cation elimination. Addition reactions are known, particularly of the polycyclic aromatic hydrocarbons, and certain substitutions of benzene systems seem best explained in terms of addition–elimination reactions.[7] In this context, IV and V can be considered products of complementary carbonium ion reactions, molecular rearrangements, which are open to alkylcyclohexadienyl cations provided a favorable balance of free energies of activation exists. The strong repulsion effects attending introduction of a second nitro group into this severely crowded system are undoubtedly the primary factors which permit successful competition of these two reactions, direct cation elimination and rearrangement followed by elimination.

That the methyl which replaces the *t*-butyl group comes from the replaced *t*-butyl group is substantiated by the observation that 2,4,6-tri-*t*-butylnitrobenzene-2,4,6-β-*t* undergoes reaction forming IV with loss of 23% of tritium activity. Theory predicts 22.2%.

The predominance of IV over V is not well understood, but it may reflect unsymmetrical charge distribution in Ia. If this is the case, the prediction is that the *p*-*t*-butyl group of I suffers rearrangement in preference to one of the *o*-*t*-butyl groups.

A further test of mechanism is clear. The proposed mechanism would strongly imply that the product distribution be altered by substitution of deuterium for aromatic hydrogen in I. Further, one would anticipate that this partitioning isotope effect would be larger than the observed kinetic isotope effect for the over-all nitration of I *vs.* I-3,5-d_2. The accompanying communication describes the results of these experiments.[8]

Acknowledgment. It is a pleasure to acknowledge the technical assistance of Terrill Rieger.

[7] (a) C. C. Price and C. T. Arntzen, *J. Am. Chem. Soc.*, **60**, 2835 (1938); (b) F. R. Mayo and W. B. Hardy, *ibid.*, **74**, 911 (1952); (b) P. B. D. de la Mare, M. Hassan, E. A. Johnson, and N. V. Klassen, *J. Chem. Soc.*, 2749 (1961); (c) P. B. D. de la Mare, R. Koenigsburger, J. S. Lomas, V. Sanchez de Olma, and A. Saxton, *Rec. Trav. Chim.*, **84**, 109 (1965); (d) P. Kovacic, C. T. Goralski, J. J. Hiller, Jr., J. A. Levisky, and R. M. Lange, *J. Am. Chem. Soc.*, **87**, 1262 (1965); (e) P. C. Myhre and G. S. Owen, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 48S.

[8] P. C. Myhre and M. Bueg, *J. Am. Chem. Soc.*, **88**, 1569 (1966).

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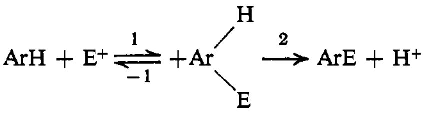
A Slow Proton Transfer in Aromatic Nitration[1]

Sir:

Steric effects are powerful factors in the determination of the relative velocity ratio, ν_2/ν_{-1}, in aromatic electrophilic substitution reactions (eq 1).[2] The essential argument is that nonbonded repulsion energy increases as a large electrophile replaces hydrogen at a confined or sterically crowded site, and that this increasing repulsion energy will manifest itself more strongly in step 2, since it is at this stage that the electrophile starts assuming product configuration.[3] It is suggested that the susceptibility of aromatic substitution reactions to steric effects represents a presently crude but useful means of ascertaining free-energy differences between steps −1 and 2 for different kinds of aromatic substitution reactions. As shown in Figure 1 the superposition of the same increasing repulsion energy term on energy profiles of "normal" aromatic substitution reactions may or may not lead to an alteration in the rate-determining step depending upon the "normal" velocity ratios, ν_2/ν_{-1}.



$$\mathrm{ArH + E^+ \underset{-1}{\overset{1}{\rightleftharpoons}} {}^+Ar\begin{matrix}\diagup H\\ \diagdown E\end{matrix} \xrightarrow{2} ArE + H^+} \qquad (1)$$

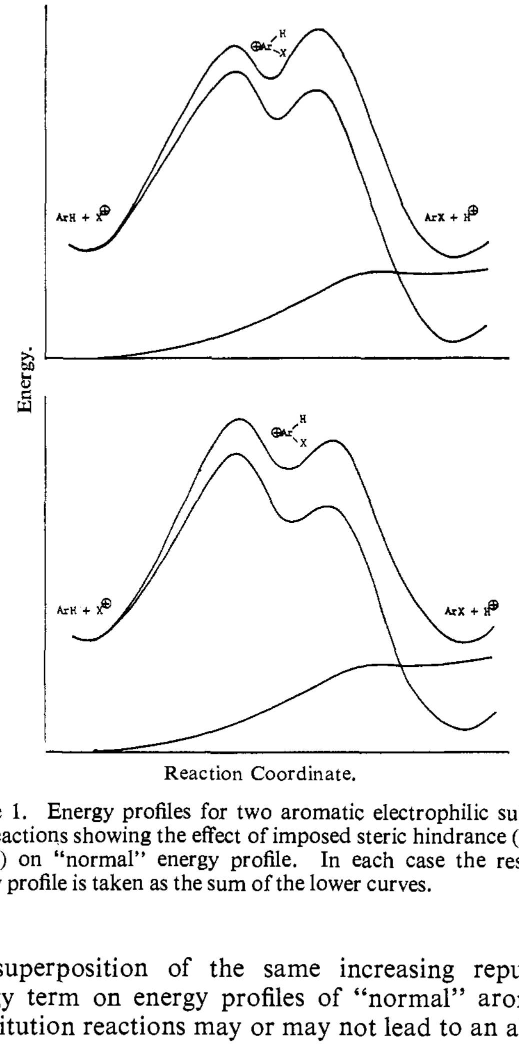


Figure 1. Energy profiles for two aromatic electrophilic substitution reactions showing the effect of imposed steric hindrance (lowest curves) on "normal" energy profile. In each case the resultant energy profile is taken as the sum of the lower curves.

The absence of an isotope effect in nitration of the very hindered 1,3,5-tri-*t*-butylbenzene, but the presence of a strong isotope effect in the positive bromination of the same hydrocarbon, indicates that these two reactions with very similar ρ values (−6.0 and −6.2) and about equivalently sized electrophiles have rather different velocity ratios.[2c] The question of importance to the construct is whether the rate ratio, ν_2/ν_{-1},

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[1] Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] (a) H. Zollinger, *Helv. Chim. Acta*, **38**, 1597, 1608, 1617, 1624 (1955); (b) W. M. Schubert and P. C. Myhre, *J. Am. Chem. Soc.*, **80** 1755 (1958); (c) P. C. Myhre, *Acta Chem. Scand.*, **14**, 219 (1960); (d) P. G. Farrell and S. F. Mason, *Nature*, **183**, 250 (1959); **197**, 590 (1963); (e) J. E. Dubois and R. Uzan, *Tetrahedron Letters*, **1965**, 309.

[3] Considerations of the effect of structure on the rate of proton transfer from the intermediate to solvent bases are also important.[2a,b]

can be bounded for nitration by finding structures possessing sufficient hindrance so that proton transfer is the rate-determining step.

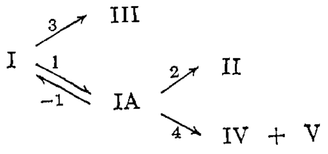
The explanation advanced to account for the formation of 2,4-dinitro-3,5-di-*t*-butyltoluene (IV) and 2,6-dinitro-3,5-di-*t*-butyltoluene (V) in addition to 1,3-dinitro-2,4,6-tri-*t*-butylbenzene (II) and 1,2-dinitro-3,5-di-*t*-butylbenzene (III) upon nitration of 2,4,6-tri-*t*-butylnitrobenzene (I) requires that proton loss from the intermediate cyclohexadienyl cation (Ia) be competitive with molecular rearrangement.[4] Barring an unusual transition state for proton loss from Ia, a partitioning isotope effect (change in product distribution) is required regardless of the over-all rate-determining step. However, additional considerations imply that, for rearrangement to become competitive with proton loss, the rate of proton loss must be considerably slower than normal. Hence, the possibility exists that the rate of proton loss from Ia may approach being the over-all rate-determining step in the formation of II. We report here experimental verification of both the requirement and the possibility.

The distribution of products upon nitration of I and I-3,5-d_2 are given in Table I. These data were obtained by chromatographic analyses (Aerograph A-90P3 SE 30, $^1/_4$ in. × 6 ft, 220°, 100 ml min^{-1}) and were found to be reproducible to within ±1%.

Table I. Product Distribution in Nitration of 2,4,6-Tri-*t*-butylnitrobenzene and 2,4,6-Tri-*t*-butylnitrobenzene-3,5-d_2

Conditions	Reactant	Products, % II	III	IV	V	$(k_H/k_D)_{II/IV}$	$(k_H/k_D)_{II/III}$
HNO_3 (90%), 0°	I	58.9	4.6	34.3	2.2	3.1	2.5
	I-d_2	32.2	6.4	58.3	3.1		
HNO_3–H_2SO_4 in CH_3NO_2 at 40°	I	81.8	3.5	13.7	1.0	3.0	2.7
	I-d_2	60.4	7.0	30.2	2.4		

Assuming the reaction scheme shown, the product ratios, $(II/IV)_H(IV/II)_D$, lead directly to the partitioning



isotope effect, $(k_H/k_D)_{II/IV}$.[5] That this isotope effect is larger than the corresponding partitioning isotope effect, $(k_H/k_D)_{II/III}$, indicates that step 1 has some kinetic importance. That is, the combined velocities of steps 2 and 4 are not too much slower than the velocity of step −1. Calculations based on present data indicate that ν_{-1}/ν_2 is equal to *ca.* 5. Further confirmation of this conclusion is obtained from direct kinetic studies. First-order rate constants for the disappearance of I and I-3,5-d_2 in nitromethane solution containing nitric acid (10.8 *M*) and sulfuric acid (0.47 *M*) at 40° were found to be 2.91 × 10^{-5} and 1.65 × 10^{-5} sec^{-1}, $(k_H/k_D)_{\text{kinetic}} = 1.8$. The calculated observed kinetic isotope effect based on product distribution data is 2.2.

Nitration of I yielding II is the first known aromatic nitration exhibiting a primary kinetic isotope effect.[6] Its occurence is in harmony with prediction. Within present error limits, the isotope effect data corroborate the reaction scheme proposed to account for the products of nitration of I.

Acknowledgment. It is a pleasure to acknowledge the technical assistance of Linda James.

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[4] P. C. Myhre and M. Beug, *J. Am. Chem. Soc.*, **88**, 1568 (1966).

[5] The assumption is implicit in this treatment that the only step sensitive to deuterium substitution is hydrogen loss from Ia yielding II.

[6] Numerous investigations of kinetic isotope effects in nitration have been conducted since the classic work of L. Melander, *Arkiv Kemi*, **2**, 211 (1950). Careful reviews and tabulations of these data have been made recently by E. Berliner, *Progr. Phys. Org. Chem.*, **2**, 157 (1964); H. Zollinger, *Advan. Phys. Org. Chem.*, **2**, 163 (1964).

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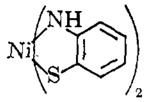
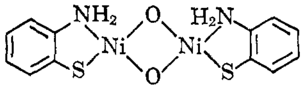
So-called Planar, Low-Spin Bis(*o*-aminobenzenethiol)cobalt(II)

Sir:

The recent suggestion[1] that the dark blue nickel complex of *o*-aminobenzenethiol should be formulated as I rather than II has prompted us to report work on some complexes of this ligand: $M^{II}(SC_6H_4NH_2)_2$, M = VO (lime green, μ_{eff} = 1.77 BM at room temperature), Cr (light blue, μ_{eff} = 4.7 BM), Mn (pale cream, μ_{eff} = 5.55 BM), Fe (pale yellow, μ_{eff} = 3.90 BM), Co (orange-brown, μ_{eff} = 4.10 BM), Ni (yellow, diamagnetic), and Zn (white, diamagnetic); $Co(SC_6H_4NH_2)_3$ (dark green, μ_{eff} = 0.5 BM); and $Cu(SC_6H_4NH_2)$ (cream, diamagnetic). The first five compounds are new and are air-sensitive. Analytical data are summarized in Table I.



I



II

The dark blue nickel compound is prepared by oxidation of yellow $Ni^{II}(SC_6H_4NH_2)_2$ in alkaline conditions.[2] Our analytical data show no oxygen to be present and so agree with I, not with the older oxygen-bridged formulation II.[2]

The cobalt(II) complex of *o*-aminobenzenethiol was reported by Livingstone[3] to be dark blue with a magnetic moment of 2.6 BM at room temperature. It has been considered a typical low-spin, planar cobalt(II) complex.[4-6] It was prepared[3] by boiling in suspension in acetone the orange-brown precipitate which ap-

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[1] E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3016 (1965).

[2] W. Hieber and R. Bruck, *Z. Anorg. Allgem. Chem.*, **269**, 13 (1952).

[3] S. E. Livingstone, *J. Chem. Soc.*, 1042 (1956).

[4] B. N. Figgis and R. S. Nyholm, *ibid.*, 338 (1959).

[5] D. H. Busch, "Cobalt," ACS Monograph 149, R. S. Young, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 6.

[6] C. M. Harris and S. E. Livingstone, "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press Inc., New York, N. Y., 1964, p 126.