phous solid had formed. The warm mixture was filtered, painstakingly excluding air and using filter-aid. The volume of the clear green n-hexane solution was reduced in vacuum to about 30 ml. The concentrated solution afforded shiny dark crystals upon cooling to Dry Ice temperature. The yield was 1.9 g. (21%) after two recrystallizations from n-hexane. The compound sublimed readily at 60°(0.1 mm.); it melted, in a sealed capillary under nitrogen, at 134–137°, with decomposition. It was stable in air for several hours, insoluble in water and readily soluble in most organic solvents such as methanol, diethyl ether, diglyme, acetone, chloroform, carbon tetrachloride and petroleum ether to give air-sensitive green solutions. *Anal.* Calcd. for $C_{10}H_7O_3V$: C, 53.12; H, 3.12; V, 22.54; mol. wt., 226.11. Found: C, 53.0; H, 3.44; V, 22.5; mol. wt., 220 (Signer method, in CH_2Cl_2).

Although these analytical results are in accord with the given composition, the alternative possibility of a cycloheptatriene-tricarbonyl-vanadium, $C_7H_8V(CO)_3$, could not be ruled out solely on this basis. Conclusive evidence for the proposed structure was furnished by the magnetic properties of the compound, whose diamagnetism is compatible only with a monomeric $C_7H_7V(CO)_3$.[7] The infrared spectrum of the compound exhibited two sharp CO stretching bands at 1915 and 1975 cm.$^{-1}$ in n-heptane solution; when taken from a KBr wafer, these absorptions were slightly shifted to 1875 and 1950 cm.$^{-1}$, respectively. Other absorptions of the KBr disk were at 785, 1430 and 3375 cm.$^{-1}$.

The given structure assignment seems to be compatible with the n.m.r. spectrum of the compound which, in $CDCl_3$ using tetramethylsilane as an internal reference, shows only a symmetrical doublet centered at 312 cps. (the individual peaks of about equal intensity being at 305 and 318 cps.).[8] The absence of the cycloheptatriene system is thus clearly indicated, although the reasons for this splitting are not fully understood at present.[9]

Tropylium-tricarbonyl-vanadium(-1) is a compound of considerable theoretical interest, being isoelectronic with the neutral complexes benzene-tricarbonylchromium(0)[10] and cyclopentadienyl-tricarbonyl-manganese($+1$)[11] as well as with the diamagnetic cations [tropylium-tricarbonyl-

chromium(0)]$^{+12}$ and [benzene-tricarbonyl-manganese($+1$)]$^{+13}$
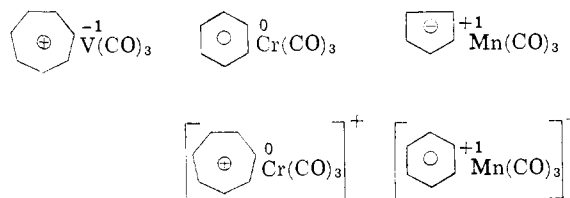
Comparison of the three neutral complexes, which contain the iso-π-electronic systems $C_7H_7^+$, C_6H_6 and $C_5H_5^-$, respectively, shows a distinct increase in stability with the decreasing electronegativity of the complexed metals, their formal oxidation states being V(-1), Cr(O) and Mn($+1$), respectively. This is well in agreement with theoretical considerations; the maximum stability, oxidatively and thermally, in this series of transition metal complexes is naturally to be expected in that case where the metal does retain a positive charge increment.[14]

Noteworthily, the reaction of [Na diglyme$_2$]-[V(CO)$_6$] with tropylium bromide, in aqueous solution as well as in isoöctane, did not furnish the described tropylium compound but yielded vanadium carbonyl and ditropyl. A similar oxidation–reduction process had been observed previously when Na[C$_5$H$_5$Cr(CO)$_3$] was treated with tropylium bromide.[1,15]
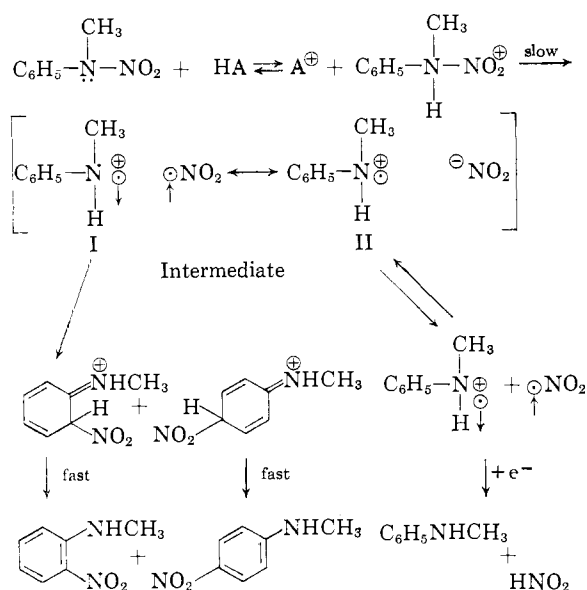
(7) We are indebted to Professor S. Kirschner at Wayne State University, Detroit, Michigan, for carrying out the magnetic susceptibility measurement.

(8) We are indebted to Mr. LeRoy F. Johnson of Varian Associates, Palo Alto, Calif., for this measurement, taken on a 60 mc. high resolution spectrometer.

(9) Following a suggestion kindly made by one of the referees, the n.m.r. spectrum was also recorded at 40 mc., in CHCl$_3$ and CS$_2$ solutions, using a spectrometer made available to us by the General Motors Technical Center, Warren, Mich. These spectra, however, showed only one wide and unresolved absorption at about 215 c.p.s. from tetramethylsilane, thus supplement the statement concerning absence of the C$_7$H$_8$ system. Since support of this statement was the principal objective of the n.m.r. spectroscopic measurements, a more complete evaluation of these data is presently considered beyond the scope of this communication.

(10) E. O. Fischer and K. Öfele, *Chem. Ber.*, **90**, 2532 (1957); B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1559). G. Natta, R. Ercoli and F. Calderazzo, *Chim. e ind.* (*Italy*), **40**, 287 (1958).

(11) E. O. Fischer and R. Jira, *Z. Naturforschg.*, **9b** 618 (1954).

(12) J. D. Munro and P. L. Pauson, *Proc. Chem. Soc.*, 267 (1959).

(13) T. H. Coffield, V. Sandel and R. D. Closson, *J. Am. Chem. Soc.*, **79**, 5826 (1957).

(14) See also P. L. Pauson, *Proc. Chem. Soc.*, 301 (1960).

(15) E. O. Fischer and H. P. Fritz, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 1, pp. 107–109, Academic Press, New York, N. Y., 1959.

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THE MECHANISM OF THE NITRAMINE REARRANGEMENT

Sir:

The acid-catalyzed rearrangement of aromatic nitramines to o- and p-nitroanilines[1] as an example of the mechanistically enigmatic, purportedly intramolecular aromatic rearrangements. Therefore, the mechanism of this process is of some theoretical interest. In order to define the course of this reaction we have intensively investigated the isomerization of N-nitro-N-methylaniline and its derivatives. The mechanism shown is consistent with our findings.

Isotope dilution analysis of the product from reaction of N-nitro-N-methylaniline-C-14 in 0.1 N hydrochloric acid at 40° indicated that 52.1% o-nitro-N-methylaniline, 30.9% p-nitro-N-methylaniline, 9.9% N-methylaniline, and *no* m-nitro-N-methylaniline were formed. This analysis was

(1) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 625–629.

Intermediate

supported by spectrophotometric measurements. In addition 13% nitrous acid was produced.

The kinetics of the reaction were followed spectrophotometrically. It was found to be first-order in both nitramine and acid. This rules out most chain processes. Specific acid catalysis was demonstrated by: (1) the constancy of reaction rate in a series of ten acetate buffers (of constant pH and ionic strength) containing from 1.2 to 27.6% acetic acid, (2) the H_0 correlation of the rates in phosphoric acid solutions (slope = 1.19), and (3) the threefold increase in rate on changing the medium from H_2O to D_2O. These facts are incorporated in the formulation of the first two steps above.

The protonated nitramine cannot lead directly to all of the observed products since the nitro group must change its position of bonding by three atoms to yield the *ortho* isomer and by five atoms to give the *para* isomer and the distances to be spanned are much too great for effective bonding to occur. Thus, an intermediate capable of proceeding to the observed products must intervene.

Evidence concerning the nature of this intermediate comes from a study of the rearrangement of N-nitro-N-methylaniline-2,6-d_2 (96.6% isotopically pure by spectral analysis) in 0.5 N hydrochloric acid at 40°. It was found that the amounts of both *o*- and *p*-nitro-N-methylaniline formed were identical with those obtained by rearrangement of ordinary N-nitro-N-methylaniline. If the nitro group first migrates to the *ortho* and then to the *para* position,[1] then the deuterium substitution would decrease the rate of the competing proton loss from the *ortho* intermediate and thus change the relative yields of the two isomers. Since no change in product composition was observed, it appears that both isomers arise from a common intermediate in which the nitro group is not bonded to the aromatic ring by a classical covalent bond.

The rates of rearrangement of thirteen *para* substituted N-nitro-N-methylanilines were correlated most satisfactorily (r = 0.99) using σ^+

constants in Hammett's equation and a value of ρ of -3.9. The latter signifies that the steps leading up to the transition state involve an over-all depletion of electrons at the reaction center. Both steps 1 and 2 as written satisfy this requirement since in the first step the electron pair on nitrogen becomes coördinated to a proton and in the second step there is formed a hybrid of structures I and II in which the amino nitrogen is deficient in one and two electrons, respectively. The σ^+ correlation demands that the electron deficiency created be situated so that it is stabilized by resonance electron donation from the substituent. This is not realized in the protonation step which would require σ or σ^- for correlation. However, the transition state of the rate-determining step will be stabilized by resonance interaction of the type correlated by σ^+.[2]

The intermediate is considered to be a radical molecular complex of the type that accounts for the anomalous behavior of radicals such as Wurster's blue and N-ethylphenazyl.[3]

Radical complexes dissociate fairly readily. Indeed, the addition of hydroquinone, α-naphthol, iodide ion, etc., resulted in a diminution in the amounts of *o*- and *p*-nitro-N-methylanilines and an increase in the proportion of N-methylaniline formed. However, the over-all rate was unaffected, indicating that the nitramine does not react with the added reagent directly. As the concentration of this substance was increased, the percentage of nitroanilines in the product decreased to a constant minimum of 56% (at 40°). Thus, the species being diverted is not the intermediate that collapses to the cyclohexadieneimines, but must be in equilibrium with it. This species appears to be free radical in nature since it reacted with the substrates mentioned above to form only N-methylaniline (40.4–43.1%) and nitrous acid (32–41%) ($C_6H_5NHCH_3^{++}$ would be expected to substitute α-naphthol). Rearrangement in the presence of aniline yielded emeraldine, a product of free radical oxidation of this amine.

The radical complex must therefore either collapse to the product-forming intermediates or dissociate to free radicals that can either be trapped or undergo secondary recombination.[4]

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(2) Thermolysis of *t*-butyl N-arylperoxycarbamates is correlated by σ^+ constants and a ρ value of -2.2 (E. L. O'Brien, F. M. Beringer, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **81**, 1506 (1959). This reaction produces an anilino radical. The arylamine portion of structure I differs from this radical only in being protonated and bearing a positive charge. Thus, the formation of an intermediate represented by structure I alone might involve a ρ value greater than -2.2. Therefore, structure II may not be required to explain the large value of ρ obtained.

(3) K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).

(4) The benzidine rearrangement formally resembles in many respects the nitramine rearrangement and may proceed by a similar mechanism.