TABLE I

THE REACTIONS OF cis- AND trans-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$ and
Co(NH$_3$)$_5$N$_3$$^{++}$ WITH Fe^{++} AT 25°, Σ (ClO$_4$$^-$) = 0.26

Complex	(Co(NH$_3$)$_4$-(N$_3$)$_2$$^+$) × 10^5, M	(Fe^{++}), M	(H$^+$), M	$k^{a,b}$, min.$^{-1}$	k_2,^{c} M^{-1} min.$^{-1}$
cis	11.8	0.0185	0.072	0.203	11.0
cis	11.8	.0185	.131	.200	10.8
cis	11.8	.0185	.189	.207	11.2
cis	7.41	.0185	.219	.210	11.3
cis	11.8	.0093	.183	.108	11.6
cis	11.8	.0370	.144	.401	10.8
trans	3.87	.0185	.072	0.190,0.193	.190^d
trans	3.87	.0185	.131	0.280	.281^d
trans	3.87	.0185	.189	.380	.369^d
trans	3.87	.0185	.219	0.416,0.411	.414^d
trans	3.87	.0093	.219	0.206	.207^d
trans	3.87	.0370	.144	.594	.600^d
·—	155^e	.148	.58	.077	.52^f
——	78^e	.074	.29	.0392	.53^f

^{a} Pseudo first-order rate constant obtained from the slope of log (D_t − D_∞) vs. time. ^{b} Corrected for the acid-catalyzed aquation^7 of Co(NH$_3$)$_4$(N$_3$)$_2$$^+$. Correction amounts to 2–6% except for experiment 5, where it is 10%. ^{c} Second-order rate constant k_2 = k/(Fe^{++}). ^{d} Calculated using the expression [4.4 + 82(H$^+$)](Fe^{++}). ^{e} The reactant is Co(NH$_3$)$_5$N$_3$$^{++}$. ^{f} Σ (ClO$_4$$^-$) = 0.89.

The observed reactivity order toward reaction with Fe^{++}, cis-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$ > trans-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$ >> Co(NH$_3$)$_5$N$_3$$^{++}$, cannot be explained invoking solely the effect of ligands trans to the bridging group^2: according to the trans effect, one would expect cis-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$ to react at approximately the same rate as Co(NH$_3$)$_5$N$_3$$^{++}$.^{3} Alternately, it could be assumed that replacement of one NH$_3$ in Co(NH$_3$)$_5$-N$_3$$^{++}$ by N$_3$$^-$, whether in the cis or trans positions, results in an increased rate of reaction with Fe^{++}, perhaps by stabilization of the Co orbital which accepts the electron.^{2,4} However, in view of the efficiency of the acid-catalyzed path for the reaction of trans-Co-(NH$_3$)$_4$(N$_3$)$_2$$^+$ with Fe^{++}, it becomes difficult to understand why acid-catalysis is not observed for the cis isomer.

We suggest, therefore, that the reaction of cis-Co-(NH$_3$)$_4$(N$_3$)$_2$$^+$ with Fe^{++} proceeds via a double-bridged activated complex entirely analogous to the one recently demonstrated for the reaction between Cr(N$_3$)$_2$$^+$ and Cr^{++}.^{5} This interpretation receives further support when the ratio of the rate constants for the reactions of cis-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$ and Co(NH$_3$)$_5$N$_3$$^{++}$ with Fe^{++} is compared with the corresponding ratio for the reactions of cis-Cr(N$_3$)$_2$$^+$ and CrN$_3$$^{++}$ with Cr^{++}. The observed ratio for the Co(III) complexes is approximately 20, and, when corrected for the difference in ionic strengths,^{6} this ratio will be close to the value of 50 observed^5 for the chromium system.

The increased reactivity of trans-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$ as compared to Co(NH$_3$)$_5$N$_3$$^{++}$ is consistent with a trans-effect in electron-transfer reactions,^{2} and the observed acid-catalysis further supports this interpretation: the N$_3$$^-$ trans to the bridging N$_3$$^-$ has a site available for a proton attachment, and movement of the

trans N$_3$$^-$ away from the Co center as electron transfer occurs^1 is facilitated by protonation.^{7}

Acid-catalyzed paths for electron-transfer reactions between metal ions, although not unprecedented, are not a common occurrence. Such paths have been observed previously in systems where addition of a proton improves the conjugation of two metal centers connected by an unsaturated bridging ligand,^{1} and for the reactions of carboxylatotetraamminecobalt(III) complexes with Cr^{++}.^{4}

(7) Facilitation of the removal of N$_3$$^-$ by protonation has been observed in other systems (A. Haim and W. K. Wilmarth, Inorg. Chem., 1, 583 (1962)) and is further supported by unpublished experiments showing that the aquations of cis- and trans-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$ between 0.2 and 1.2 M H$^+$ are first order in complex and first order in H$^+$, with undetectable contributions of H$^-$ independent paths.

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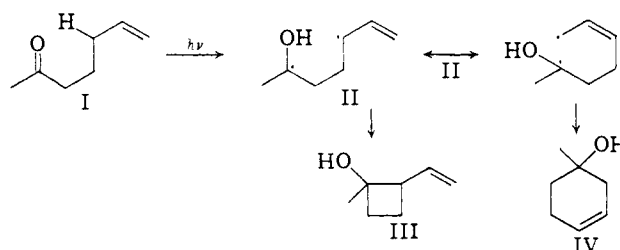UNIVERSITY PARK, PENNSYLVANIA

ON THE MECHANISM OF PHOTOCHEMICAL FORMATION OF CYCLOBUTANOLS

Sir:

Aliphatic ketones containing γ-hydrogen upon irradiation with ultraviolet light in solution undergoes two concurrent reactions, the type II cleavage^1 and the formation of cyclobutanols.^{2} Both reactions appear to be intramolecular with little or no detectable side reactions.^{3} In the cases of 2-octanone and 20-ketosteroids, two isomeric cyclobutanols are obtained.^{4} Two mechanisms have been proposed for the photochemical formation of cyclobutanols, one a step-wise mechanism^2 (eq. 2) and the other a concerted mechanism^5 (eq. 3). On the basis of available experimental data, these two mechanisms cannot be differentiated.
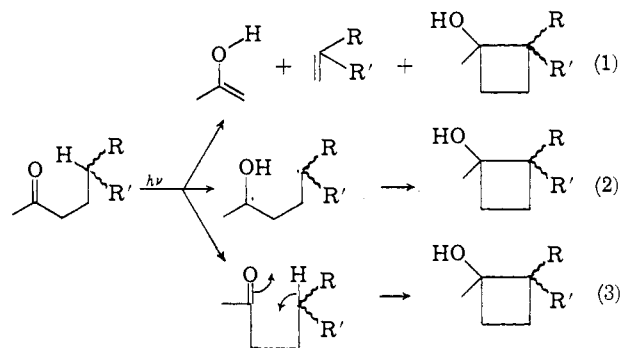
The irradiation of 6-hepten-2-one [I] was undertaken in order to provide direct evidence as to the mechanism of the cyclobutanol formation. Should the reaction proceed by a concerted mechanism, the products would contain only cyclobutanols. However, if the intermediate is a free radical, an allyl radical [II] in this

(2) L. Orgel, Report of the Tenth Solvay Conference, Brussels, 1956, p. 289.

(3) It is not likely that the increased reactivity of the cis complex as compared to Co(NH$_3$)$_5$N$_3$$^{++}$ is a consequence of the decrease in charge. Thus, CrF^{--} reacts with Cr^{++} at a faster rate than cis- or trans-CrF$_2$$^+$ (Y. T. Chia and E. L. King, Discussions Faraday Soc., 29, 109 (1960)). Furthermore, an equilibrium mixture of cis- and trans-Co(NH$_3$)$_4$OH$_2$ N$_3$$^{++}$ reacts with Fe^{++} in 1.2 M HClO$_4$ 70 times faster than Co(NH$_3$)$_5$N$_3$$^{++}$ (A. Haim, unpublished results). See also ref. 4.

(4) K. D. Kopple and R. R. Miller, Proc. Chem. Soc., 306 (1962).

(5) R. Snellgrove and E. L. King, J. Am. Chem. Soc., 84, 4610 (1962).

(6) The reactions of cis-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$ and Co(NH$_3$)$_5$N$_3$$^{++}$ were studied at Σ (ClO$_4$$^-$) values of 0.26 and 0.89, respectively.

(1) R. G. W. Norrish, Trans. Faraday Soc., 33, 1521 (1937).

(2) N. C. Yang and D. H. Yang, J. Am. Chem. Soc., 80, 2913 (1958).

(3) W. Davis, Jr., and W. A. Noyes, Jr., ibid., 69, 2153 (1947); P. Ausloos and R. E. Rebbert, ibid., 83, 4897 (1961).

(4) N. C. Yang and D. H. Yang, Tetrahedron Letters, 4, 10 (1960); O. Jeger, et al., Helv. Chim. Acta, 43, 351 (1960).

(5) O. Jeger, et al., ibid., 42, 2122 (1959).

case, it may cyclize in two possible manners to form methylvinylcyclobutanols [III] as well as methylcyclo-hexenol [IV] according to the following scheme:

When a solution of 6-hepten-2-one in pentane was irradiated with a low pressure mercury resonance quartz lamp,[6] acetone (32%), butadiene (23%) and an alcohol fraction (7.5%) isomeric with the starting ketone (found: C, 74.63; C, 10.48) were formed among some unreacted ketone (20%) and high molecular weight material. The major alcohol (6%), separated by gas chromatography, was identified to be 1-methyl-2-vinylcyclobutanol [III] (found: C, 74.88; H, 10.77; n^{25}D 1.4598; γ_{max} 3320, 3060, 1635, 990 and 910 cm.$^{-1}$). The n.m.r. spectrum exhibits a singlet at 8.85 τ ($-CH_3$), a multiplet at 7.90–8.70 τ ($-CH_2$), a quartet at 7.15 τ (allylic), a singlet at 6.56 τ ($-OH$), a triplet at 5.52, 5.10 and 4.93 τ (terminal vinyl) and a multiplet at 3.50–4.45 τ (non-terminal vinyl) and the relative intensities of these peaks are 3:4:1:1:2:1, respectively. Its double bond region in the n.m.r. spectrum was essentially identical with that of a known allyl system.[7] The other alcohol component (1.4%) had been identified tentatively to be 1-methyl-3-cyclohexenol [IV], γ_{max} 3320 and 3005 cm.$^{-1}$; 8.80 τ (singlet, $-CH_3$) and 4.42 τ (singlet, vinylene). Upon hydrogenation the alcohol fraction absorbed one mole equivalent of hydrogen, and the hydrogenated mixture was separated by gas chromatography into 1-methyl-2-ethylcyclobutanol[8] and 1-methylcyclohexanol in 4:1 ratio, identical in all respects with the corresponding authentic samples.

The isolation of both III and IV in the present investigation conclusively substantiates the step-wise mechanism.[2] It also indicates that the reactive state responsible for this reaction may be a triplet since the intermediate radical was free to delocalize over an allylic system.[9]

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(6) M. S. Kharasch and H. N. Friedlander, J. Org. Chem., 14, 245 (1949).

(7) Varian N.m.r. Spectra Catalog, spectrum No. 136.

(8) Prepared by the photochemical reaction of 2-heptanone, D. H. Yang, unpublished result.

(9) G. S. Hammond, Abstracts of Papers, 17th National Organic Chemistry Symposium of the American Chemical Society, 1961, pp. 48–58.

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## IONIZATION POTENTIAL OF BENZYNE

Sir:

The chemistry of benzyne (1,2-dehydrobenzene) in solution has received considerable attention, and has been reviewed by a number of authors.[1] Recently, the transient spectrum of an intermediate has been observed in the flash photolysis of o-iodophenylmercuric iodide and other precursors,[2] which is almost certainly attributable to benzyne. We wish to report the detection of benzyne in the thermal decomposition of 1,2-diiodobenzene in a reactor coupled to a mass spec-

(1) G. Wittig, Angew. Chem., 69, 245 (1957); J. D. Roberts, Chem. Soc. (London) Spec. Publ., 12, 115 (1958); R. Huisgen, in "Organometallic Chemistry," H. H. Zeiss, Ed., Reinhold Publishing Co., New York, N.Y., 1960; H. Heaney, Chem. Rev., 62, 81 (1962).

(2) R. S. Berry, G. N. Spokes and R. M. Stiles, J. Am. Chem. Soc., 82, 5240 (1960); 84, 3570 (1962).

trometer.[3] The detection of free radicals and other products is carried out by ionization of a portion of the product stream with electrons of low energy, such that only parent ions are formed. The thermal decomposition of 1,2-diiodobenzene in this reactor at 960° (residence time $\sim 10^{-3}$ sec., pressure $\sim 10^{-3}$ mm.) leads to the formation of the following products: iodine atoms, iodophenyl radicals, phenyl iodide, phenyl radicals, benzene, a product of parent mass 76 and a product of parent mass 152. The reactions giving rise to these products are thought to be
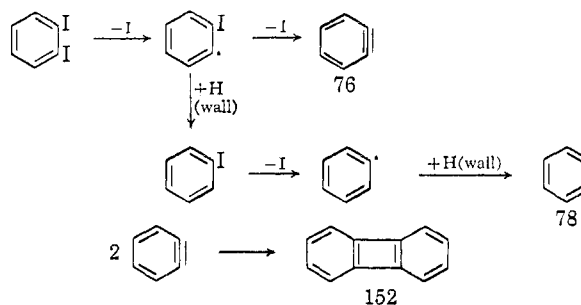
These reactions are similar to those reported in the photolysis of 1,2-diiodobenzene in solution.[4] A comparison of the ionization efficiency curves for benzene, the product of mass 76 and an added xenon standard leads to the vertical ionization potentials: benzene, 9.50 v.; mass 76, 9.75 v. Identification of this species of mass 76 as benzyne by its parent mass alone is not sufficient, since three other structures for C_6H_4 hydrocarbons can be written: $HC\equiv CCH=CHC\equiv CH$ (I), $H_2C=C=C=C=C=CH_2$ (II) and $H_2C=C=C=CHC\equiv CH$ (III). Formation of any of these three species from 1,2-diiodobenzene appears quite improbable. Formation of I would require one H-atom to migrate to a next-but-one carbon, II and III require the migration of two H-atoms. Moreover, the identity of the product of mass 76 with any of these can be ruled out on the basis of the expected ionization potentials. II and III, being substituted butatrienes, will have ionization potentials less than that of butatriene itself, 9.28 v.[5] The ionization potential of I can be estimated sufficiently closely for the present purposes by comparing the changes in ionization potential along the two series: ethylene, propylene, 2-butene; and ethylene, vinylacetylene and I. Substitution of H in ethylene by $-C\equiv CH$ decreases the ionization potential slightly less (0.72 v.) than substitution by $-CH_3$ (0.78 v.).[6] Comparison with 2-butene, derived from ethylene by a 1,2-disubstitution, gives the ionization potential of I to be 9.40 v. The observed value for mass 76 is clearly larger than expected values for I, II or III.

The thermal decompositions of 1,4- and 1,3-diiodobenzene under the same conditions were also examined. The former produced iodophenyl radicals, benzene, and again a compound of mass 76, but no product of mass 152. The ionization potential of the species of mass 76 in this case, however, was 9.46 v., in good agreement with the estimated value for I. The course of this reaction is evidently
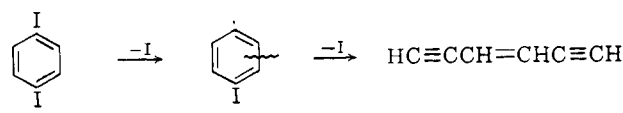
(3) J. B. Farmer and F. P. Lossing, Can. J. Chem., 33, 861 (1955); F. P. Lossing, P. Kebarle and J. B. de Sousa in "Advances in Mass Spectrometry," Pergamon Press, London, 1959, p. 431.

(4) J. A. Kampmeier and E. Hoffmeister, J. Am. Chem. Soc., 84, 3787 (1962).

(5) A. Streitwieser, Jr., ibid., 82, 4123 (1960).

(6) R. E. Honig, J. Chem. Phys., 16, 105 (1948).