TABLE I

PRODUCTS OF THE BASE HYDROLYSIS OF *cis*-AND *trans*-$[Co(en)_2AX]^{n+}$

Reactant		Product	% *cis*	Ref.
trans-$[Co(en)_2ClBr]^+$	→	$[Co(en)_2ClOH]^+$	5 (±5)[a]	*c*
trans-$[Co(en)_2ClCl]^+$	→	$[Co(en)_2ClOH]^+$	5 (±2)	*c*
trans-$[Co(en)_2N_3NCS]^+$	→	$[Co(en)_2NCSOH]^+$	70	*d*
trans-$[Co(en)_2ClNCS]^+$	→	$[Co(en)_2NCSOH]^+$	76	*e*
trans-$[Co(en)_2BrNCS]^+$	→	$[Co(en)_2NCSOH]^+$	81 (±3)	*e*
trans-$[Co(en)_2BrOH]^+$	→	$[Co(en)_2OHOH]^+$	90 (±2)	*c*
trans-$[Co(en)_2ClOH]^+$	→	$[Co(en)_2OHOH]^+$	94 (±2)	*c*
trans-$[Co(en)_2ClNO_2]^+$	→	$[Co(en)_2NO_2OH]^+$	6 (±3)	*f*
trans-$[Co(en)_2NCSNO_2]^+$	→	$[Co(en)_2NO_2OH]^+$	10	*g*
trans-$[Co(en)_2N_3Cl]^+$	→	$[Co(en)_2N_3OH]^+$	27[b] (13)	*h*
trans-$[Co(en)_2N_3N_3]^+$	→	$[Co(en)_2N_3OH]^+$	30 (±5)	*h*
trans-$[Co(en)_2N_3NCS]^+$	→	$[Co(en)_2N_3OH]^+$	60??	*d*
cis-$[Co(en)_2ClBr]^+$	→	$[Co(en)_2ClOH]^+$	30 (±5)	*c*
cis-$[Co(en)_2ClCl]^+$	→	$[Co(en)_2ClOH]^+$	37 (±2)	*c*
cis-$[Co(en)_2ClNO_2]^+$	→	$[Co(en)_2NO_2OH]^+$	67 (±7)	*f*
cis-$[Co(en)_2NCSNO_2]^+$	→	$[Co(en)_2NO_2OH]^+$	55	*g*
cis-$[Co(en)_2ClNH_3]^{+2}$	→	$[Co(en)_2NH_3OH]^{+2}$	84	*i*
cis-$[Co(en)_2BrNH_3]^{+2}$	→	$[Co(en)_2NH_3OH]^{+2}$	85	*i*
cis-$[Co(en)_2NO_3NH_3]^{+2}$	→	$[Co(en)_2NH_3OH]^{+2}$	86	*i*
cis-$[Co(en)_2ClOH]^+$	→	$[Co(en)_2OHOH]^+$	97 (±2)	*c*
cis-$[Co(en)_2BrOH]^+$	→	$[Co(en)_2OHOH]^+$	96 (±2)	*c*
cis-$[Co(en)_2N_3Cl]^+$	→	$[Co(en)_2N_3OH]^+$	59[b] (51)	*h*
cis-$[Co(en)_2N_3N_3]^+$	→	$[Co(en)_2N_3OH]^+$	55 (±5)	*h*
cis-$[Co(en)_2N_3NCS]^+$	→	$[Co(en)_2N_3OH]^+$	100??	*d*
cis-$[Co(en)_2NCSCl]^+$	→	$[Co(en)_2NCSOH]^+$	80	*h, i*
cis-$[Co(en)_2NCSN_3]^+$	→	$[Co(en)_2NCSOH]^+$	70	*d*

[a] The values in parentheses are from the original reference. [b] Values recalculated using ϵ 110 for *trans*-$[Co(en)_2N_3OH_2]^{+2}$ (D. A. Loeliger and H. Taube, to be published). [c] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962). [d] P. J. Staples, *ibid.*, 3227 (1963). [e] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *ibid.*, 1691 (1956). [f] S. Asperger and C. K. Ingold, *ibid.*, 2862 (1956). [g] A. Roger and P. J. Staples, *ibid.*, 4749 (1963). [h] P. J. Staples and M. L. Tobe, *ibid.*, 4803 (1960). [i] R. S. Nyholm and M. L. Tobe, *ibid.*, 1707 (1956).

mediate although they could vary from one type of intermediate to the next.[3c]

In this context the data in Table I are arranged to show the remarkable agreement between the concentrations of isomeric products from different parents where a common intermediate is conceived for the SN1CB mechanism.

Some comment is needed on the accuracy of the numbers in Table I, particularly for the reactions *cis*- and *trans*-$[Co(en)_2N_3NCS]^+ \rightarrow [Co(en)_2N_3OH]^{2+}$. In both instances the method of analysis of the complex mixture is insensitive to the product composition and these apparent exceptions may well conform to the general agreement above. The same comment is true, although to a lesser extent, for the product analysis from *cis*- and *trans*-$[Co(en)_2N_3NCS]^+ \rightarrow [Co(en)_2NCSOH]^+$ and *cis*-$[Co(en)_2NCSNO_2]^+ \rightarrow [Co(en)_2NO_2OH]^+$. In addition the product composition for the reactions *cis*- and *trans*-$[Co(en)_2ClN_3]^+ \rightarrow [Co(en)_2N_3OH]^+$ was redetermined using the extinction coefficient (110) for *trans*-$[Co(en)_2N_3OH_2]^{2+}$ obtained by Loeliger and Taube,[5] and the recalculated values are in better agreement with the products from *trans*-$[Co(en)_2(N_3)_2]^+$ than formerly.

This communication was prompted by some recent studies on the catalyzed aquation of some of the bis-(ethylenediamine) disubstituted cobalt(III) complexes[5,6] where the same stereochemical products were obtained from different sources and a common intermediate was proposed. So far the stereochemical results for base hydrolysis also are consistent with the production of a five-coordinate intermediate; it will now be interesting to see what effect the temperature has on the product distribution and also if the correlation holds over a wider range of leaving groups.

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RECEIVED SEPTEMBER 14, 1964

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(5) D. A. Loeliger and H. Taube, to be published.

(6) A. M. Sargeson, *Australian. J. Chem.*, **17**, 385 (1964).

A Simple Molecular Orbital Description of the Charge-Transfer Spectra of Some Substituted Borazines

Sir:

From a study of π-complexes, Muzskat and Kirson[1] have inferred the following order of ionization potentials: $1,3,5\text{-}(C_6H_5)_3C_6H_3 < (C_6H_5NBH)_3 < (C_6H_5BNH)_3$. In addition, the relative ionization potentials, $(C_6H_5NBCH_3)_3 < (C_6H_5BNCH_3)_3$, probably holds because the latter compound in the presence of tetracyanoethylene does not display a visible charge-transfer band while the former does.[1] Muzskat and Kirson employed a variety of steric, inductive, and resonance arguments to explain the observed orders. Our previous success in the correlation of reduction potentials of phenyl-substituted borazines with Hückel molecular orbital calculations[2] led us to apply a similar treatment to the present problem.

Within the framework of simple MO theory the ionization potential is equal to the energy of the highest filled π-molecular orbital; this energy is easily calculated, providing sufficient information is available to establish values for the Coulomb and resonance integrals. In the present calculations we employed parameters h_B, h_N, and k_{BN} which had been used to fit reduction potentials of phenylborazines.[2] In addition, k_{CB} (inter-ring) and k_{CN} (inter-ring) were varied by cos θ,[3] where the twist angle (θ) was assigned a variety of values which encompass our previous estimate of 20°, based on analogy with biphenyl, and also Muzskat and Kirson's estimates, based on molecular models. As these authors have pointed out the choice of θ is not highly critical for qualitative discussions of relative energies. The problem of how to include methyl substituent effects on borazine has not been investigated by Hückel MO methods. However, Kaufman and Hamann have presented arguments in favor of employing methyl substituent parameters determined for hy-

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(1) K. A. Muzskat and B. Kirson, *Israel J. Chem.*, **2**, 57 (1964).

(2) D. F. Shriver, D. E. Smith, and P. Smith, *J. Am. Chem. Soc.*, **86**, 5153 (1964).

(3) The extent of overlap is proportional to cos θ. In their use of $\cos^2 \theta$ Muzskat and Kirson appear to misinterpret a paper by Dewar [*J. Am. Chem. Soc.*, **74**, 3345 (1952)] in which it is shown that the resonance energy is proportional to $\cos^2 \theta$ for certain conjugated systems. The resonance energy is determined from the total π energy of a conjugated system and is not pertinent to a discussion of ionization potentials, which depend on the energy of a single level.

TABLE I

COMPARISON OF MUZSKAT AND KIRSON'S IONIZATION POTENTIAL DATA WITH CALCULATED ENERGIES

Compound	Ionization potential,[a] e.v.	θ, deg.	Energy of highest filled π-level[b]
1,3,5-$(C_6H_5)_3C_6H_3$	8.21	20.0	0.726
$(C_6H_5NBH)_3$	8.36	20.0	0.680
		39.6	0.745
		44.2	0.766
$(C_6H_5BNH)_3$	8.92	20.0	0.982
		39.6	0.987
		44.2	0.988
$(C_6H_5NBCH_3)_3$	9.16	71.6	0.925 (0.842)[c]
		72.2	0.929 (0.847)
$(C_6H_5BNCH_3)_3$	?[d]	71.6	0.997 (0.936)
		72.2	0.998 (0.938)

[a] Ref. 1. [b] Calculated for $h_N = -h_B = 0.890$, $k_{B-N} = 0.855$, $k_{B-C} = 0.618 \cos\theta$, and $k_{N-C} = 0.915 \cos\theta$. The latter two parameters refer to inter-ring bonds. These energies are in units of β_{CC}, which is negative, and are referred to α_C (the Coulomb integral for carbon) = 0. [c] Values in parentheses include an inductive parameter for an attached methyl group $\delta h = -0.54$. When the inductive effect is included k_{B-N} is scaled according to the Wolfsberg–Helmholtz approximation (see ref. 2). [d] As noted in the text this ionization potential is probably higher than that of $(C_6H_5NBCH_3)_3$. This inference is based on the lack of a visible charge-transfer band for $(C_6H_5BNCH_3)_3$. It is also possible that the charge-transfer band was not observed because it falls at very low energies, or because a complex was not formed. In view of the widespread occurrence of tetracyanoethylene complex formation and the high energy of the charge-transfer complexes of substituted borazines, the original interpretation is the most reasonable.

drocarbons in calculations with B or N compounds.[4] Therefore, we did one set of calculations for the methyl-substituted compounds in which a change in h of -0.54[5] was made for atoms attached to methyl, and another set with no methyl inductive effect; the results are given in Table I.

Providing we compare similar compounds the Hückel calculations give the correct orders for energies of the highest filled molecular orbitals: $(C_6H_5NBH)_3 > (C_6H_5BNH)_3$ and $(C_6H_5NBCH_3)_3 > (C_6H_5BNCH_3)_3$. Also, calculated energies and observed ionization potentials for the former pair lead to $\beta_{CC} = 2.2 \pm 0.3$ e.v., which is within the range observed for conjugated hydrocarbons.[6] The Hückel MO treatment appears to provide a simple means of interpreting the charge-transfer spectra without invoking Muzskat and Kirson's assumption that the N-phenyl group has a larger electron-donating effect than an N-methyl group. Evidence to the contrary is readily available from Taft σ^* values (CH_3–, 0.00; C_6H_5–, 0.60),[7] empirical electronegativities (CH_3– < C_6H_5–),[7] and semi-empirical orbital electronegativities (2.48 for sp^3 and 2.75 for an sp^2 carbon hybrid orbital).[8]

There is little doubt that an adjustment of molecular orbital parameters could lead to a single correlation series for the MO energies and ionization potentials of triphenylbenzene and all of the substituted borazines, but this parameter fitting cannot be checked with the limited data now available. Furthermore, steric hindrance of complex formation with tetracyanoethylene is probably much different for triphenylborazines than for trimethyltriphenylborazines. The resulting variation in donor–acceptor interaction will be reflected in derived ionization potentials and will probably invalidate comparison of these ionization potentials for the two groups. Hückel MO theory does offer a satisfactory answer to the question: What is the effect of B-phenyl *vs.* N-phenyl substitution on ionization potentials and electron affinities of the borazines? In addition, the MO treatment, like resonance theory, reveals a lower B–N bond order for N-triphenylborazine than B-triphenylborazine, and this is in harmony with results of pyrolysis experiments.[9]

Acknowledgment.—This research was supported by the Department of Defense through the Northwestern University Materials Research Center, and also by the N.S.F. We thank the University Computing Center for computer time.

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RECEIVED OCTOBER 12, 1964

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(4) J. J. Kaufman and J. R. Hamann, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p. 95.

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(6) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., Chapter 7.

(7) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1963, section 2.2.

(8) H. H. Jaffé and J. Hinze, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(9) H. C. Newsom, W. D. English, A. L. McCloskey, and W. G. Woods, *ibid.*, **83**, 4134 (1961).

Book Reviews

Inorganic Thermogravimetric Analysis. Second and Revised Edition. By CLEMENT DUVAL (translated by Ralph E. Oesper). American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York 17, N. Y. 1963. xv + 722 pp. 15 × 22.5 cm. Price, $22.00.

This book is the second and revised edition of the earlier classical edition which appeared in 1952. It is now generally agreed that the first edition did much to kindle the interest of analytical and inorganic chemists in the area of thermogravimetry. As a result of this interest, a large number of papers have appeared in this area of research since the first edition. In fact, Professor Duval states in the preface that some 2200 papers in periodicals were read in the preparation for the second edition.

The contents of the book are divided into two main parts: (a) thermobalances and (b) thermolysis curves. Although practically every thermobalance is mentioned in part a, the contents are now generally of historical interest only because of the recent developments in instrumentation during the past 3 years. A good discussion is presented on the applications of thermobalances (Chapter 4), but kinetic studies are absent. Of even more interest is the list of precautions to be taken in interpreting