Table I. (H_2,H_2) Exchange Rate Constants at 1600°K (cm^3/mole sec)

v	v'	k_{st}	k_B
0	0	3.438×10^4	3.268×10^4
0	1	1.009×10^6	2.397×10^4
1	1	1.634×10^7	9.695×10^3
0	2	1.521×10^7	1.117×10^4
1	2	1.535×10^8	2.816×10^3
0	3	1.530×10^8	4.285×10^3

obtained (*e.g.*, $K(T)$ is 1.332×10^5 cm^3/mole sec at 1600°K and 1.164 cm^3/mole sec at 1000°K). The values of $K(T)$ are well fitted by an Arrhenius plot with an activation energy (E_a) of 61.64 kcal/mole and a preexponential factor (A) of 3.475×10^{13} cm^3/mole sec. Thus, E_a is only slightly less than the classical barrier height. The absolute rate theory values of the rate constants for the same surface are somewhat smaller than those from the trajectory treatment (*e.g.*, $K(T)$ is 0.643×10^5 cm^3/mole sec at 1600°K and 0.296 cm^3/mole sec at 1000°K).

Comparison of our results with the conclusions of Bauer, *et al.*,[2,3] shows agreement in that the rate of H_2,H_2 exchange is greatly enhanced for molecules in excited vibrational states (v and/or $v' > 0$) as compared with molecules in the ground vibrational state ($v = v' = 0$), the translational and rotational degrees of freedom having thermal distributions; *e.g.*, k_{st} ($v = 0$, $v' = 1$) is ~30 times k_{st} ($v = 0$, $v' = 0$) at $T_{tr} = T_{rot} = 1600$°K. However, because of the low population of the excited states, the contribution to $K(T)$ from the ($v = 0$, $v' = 1$) collisions is only 0.74 that from the ($v = v' = 0$) collisions at 1600°K and becomes even less at lower temperatures. By summing over the k_B values at 1600°K, one finds that k_B ($v = v' = 0$) contributes ~25% and all of the excited states 75% of $K(T)$.

Thus, in contrast to the suggestion of Bauer, *et al.*,[2,3] there is no theoretical evidence for a "vibrational threshold." Model calculations show that an increase in the vibrational energy availability is by itself not sufficient to produce such a threshold;[10] the translational energy must be significantly *less* effective as well. Since corresponding results are obtained in calculations on the H_2,D_2 system, further studies are clearly needed to resolve the differences between ref 2 and 3 and the present treatment.

The calculations reported here are only illustrative because they are based on classical mechanics and employ an approximate potential surface. Thus, it is possible that the results do not provide an accurate description of the H_2,H_2 reaction. However, although the absolute value of the rate constant is very sensitive to the potential, particularly to the barrier height, the relative k_{st} and k_B values are much less so. Moreover, it is likely that the calculated efficiency of translational and vibrational energy in overcoming the activation barrier is not atypical for systems in which the reactants and products are similar. For significantly different values, a drastic modification of the potential surface would be required.[11] In more asymmetric reactions (*e.g.*, some endothermic reactions), vibrational energy may have increased importance. An example might be "late-uphill" surface corresponding to CH_3 + KI → K + CH_3I, the inverse of the reaction for which molecular beam studies[12] indicate that much of the exothermicity appears as internal excitation of products. However, even in this case the available data when combined with microscopic reversibility arguments are not sufficient to show that the excited vibrational states would dominate the reaction for an equilibrium population in the thermal region. For the nonequilibrium case with an excess of excited molecules, there are likely to be measurable effects for reactions involving a significant activation energy and/or endothermicity. It would be of great interest to have more data on exchange reactions with a non-Boltzmann vibrational population produced by the stimulated Raman effect,[13] "chemical activation,"[14] or electron impact.[15]

A more detailed analysis of the H_2,H_2 and H_2,D_2 exchange reactions and related high-energy processes (*i.e.*, dissociation, exchange dissociation, atomization) will be presented.

Acknowledgment. We wish to thank Dr. S. Bauer, Dr. S. Byron, Dr. G. B. Kistiakowsky, Dr. J. Kiefer, and Dr. R. D. Kern for helpful discussion. We gratefully acknowledge the machine time used for these calculations at the Columbia Computing Center.[16]

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(10) A vibrational threshold value v_0 would be defined to exist at a temperature T if

$$\sum_{v'=0}^{v_0} k_B(v_0 - v', v', T) \gg \sum_{v'' \geqslant v'=0}^{v_0-1} k_B(v'' - v', v', T) \approx 0$$

(11) Distortions in the surface such that the reaction trajectory is perpendicular to the initial direction of translational motion while climbing the potential barrier could increase the vibrational–translational efficiency ratio. The distortions discussed in ref 7 are unlikely to be of this type; however, if the barrier were as high as in ref 7, an atomic mechanism would be expected.

(12) D. R. Herschbach, *Advan. Chem. Phys.*, **10**, 319 (1966).

(13) F. De Martini and J. Ducuing, *Phys. Rev. Letters*, **17**, 117 (1966).

(14) B. S. Rabinovitch and M. C. Flowers, *Quart. Rev.* (London), **18**, 122 (1964).

(15) H. von Koch and L. Friedmann, *J. Chem. Phys.*, **38**, 1115 (1963); T. Moran and L. Friedmann, *ibid.*, **39**, 2491 (1963). Although a vibrational threshold is suggested for the endothermic reaction He + H_2^+ → HeH^+ + H, it is not clear that the data require more than a significant change in the reaction cross section with H_2^+ vibrational state. See also J. C. Light and J. Lin, *J. Chem. Phys.*, **43**, 3209 (1965), and J. H. Futrell and F. P. Abramson in "Ion-Molecule Reactions in the Gas Phase," Advances in Chemistry Series No. 58, American Chemical Society, Washington, D. C., 1966, Chapter 8.

(16) Most of the computations were performed while the authors were at Columbia University.

(17) National Science Foundation (1965–1966) and National Institutes of Health (1966–1967) Postdoctoral Fellow.

K. Morokuma, L. Pedersen,[17] M. Karplus
Department of Chemistry, Harvard University
Cambridge, Massachusetts

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Cobalt(III) Complexes of Linear Tetramines. II. Isomerism in the *trans*-Dichloro(1,4,8,11-tetraazaundecane)cobalt(III) Ion

Sir:

Quite recently, Sargeson and co-workers have demonstrated the configurational stability of coordinated asymmetric secondary nitrogen by isolating isomers of cobalt(III) complexes which differ in the configuration about such nitrogen atoms within the complexes.[1] In light of their work, our investigations of cobalt(III) complexes of 1,4,8,11-tetraazaundecane (2,3,2-tet),

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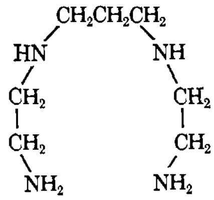
(1) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967), and references therein.

structure I, have provided results which are very informative with respect to the stereochemistry of coordination compounds. Herein, we wish to report these results.



I

trans-[Co(2,3,2-tet)Cl$_2$]$^+$, prepared by the standard air-oxidation technique,[2,3] undergoes mercury(II)-induced aquation in acidic solution to yield a mixture of products which can be separated into four fractions on a column of Dowex 50W-X2 cation-exchange resin. Two of these fractions have been identified in solution as *trans*-[Co(2,3,2-tet)(H$_2$O)Cl]$^{2+}$. Referring to Figure 1, which shows the most stable configurations for 2,3,2-tet in *trans* structures using a projection technique,[4] it is evident that there are four possible isomers of *trans*-[Co(2,3,2-tet)(H$_2$O)Cl]$^{2+}$: the two geometrical *RS*(*meso*) isomers, resulting from the nonequivalence of the two *trans* sites in the *RS* case, and the *RR* and *SS* antipodes. The configurations about the asymmetric nitrogen atoms in the *trans*-chloroaquo products can be related to the configurations in the *trans*-dichloro complex, from which the chloroaquo products were obtained, in the following way. Both products undergo chloride anation quantitatively in a mixture of hydrochloric and perchloric acids to yield sparingly soluble *trans*-[Co(2,3,2-tet)Cl$_2$]ClO$_4$ salts which exhibit infrared spectra indistinguishable from each other as well as *trans*-[Co(2,3,2-tet)Cl$_2$]ClO$_4$ prepared by the air-oxidation technique. Since the configurational integrity of coordinated asymmetric secondary nitrogen atoms is maintained in acid solution,[1] no configurational change should occur under the conditions of the aquation reaction, the anation reaction, or the separation procedure. Thus, the only conclusions compatible with these considerations and the above results is that the *trans*-[Co(2,3,2-tet)Cl$_2$]$^+$ ion is the pure *RS*(*meso*) isomer and the *trans*-[Co(2,3,2-tet)(H$_2$O)Cl]$^{2+}$ complexes are the geometrical isomers predicted for the *RS*(*meso*) configuration.[5] If the *trans*-[Co(2,3,2-tet)Cl$_2$]$^+$ had consisted of the *RR*,*SS* racemate in addition to the *RS*(*meso*) isomer, the *trans*-(*RR*,*SS*)-chloroaquo complexes would have had to be present in one of the two chloroaquo fractions obtained since the other two fractions were found to contain only dichloro and diaquo complexes. The *trans*-[Co(2,3,2-tet)Cl$_2$]$^+$ complexes prepared by anation would then have been different for the two fractions, which is inconsistent with the above results.

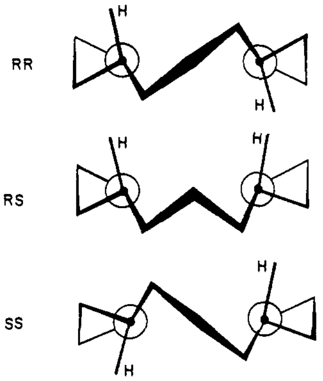


Figure 1. Configurations of 1,4,8,11-tetraazaundecane in *trans* octahedral structures.

Cobalt(III) complexes of 2,3,2-tet having the *cis* structure can be prepared using bidentate ligands to occupy *cis* octahedral sites in the complexes. Such a complex, *cis*-[Co(2,3,2-tet)CO$_3$]Cl, can be prepared by reaction of *trans*-(*RS*)-[Co(2,3,2-tet)Cl$_2$]Cl with Na$_2$CO$_3$ in aqueous solution. Molecular models suggest that for *cis* structures the *RR* and *SS* configurations are preferred in the β case and necessary in the α case. Since the basic conditions under which the carbonato complex is prepared should permit rearrangement about the asymmetric nitrogen atoms, the *RR* and *SS* configurations are expected for the *cis*-carbonato complex. The carbonato complex undergoes acid hydrolysis in concentrated hydrochloric acid, under which conditions the configurations about the secondary nitrogen atoms should be retained, to yield *cis*-[Co(2,3,2-tet)Cl$_2$]$^+$ which isomerizes, producing a mixture of the *cis* isomers as well as the *trans* isomer. Because of the low solubility of the perchlorate salt of the *trans*-dichloro complex, it can be readily isolated from the mixture. Although the complex so obtained and *trans*-(*RS*)-[Co(2,3,2-tet)Cl$_2$]ClO$_4$ exhibit indistinguishable visible spectra,[6] their infrared spectra[7] are markedly different, which confirms the notion that the former is the *RR*,*SS* racemate.

Thus we have been able to prepare *trans*-(*RR*,*SS*)-[Co(2,3,2-tet)Cl$_2$]ClO$_4$[8] and *trans*-(*RS*)-[Co(2,3,2-tet)Cl$_2$]-ClO$_4$ by kinetic and thermodynamic routes, respectively. These diastereomers exhibit strikingly different chemical behavior. First, *trans*-(*RR*,*SS*)-[Co(2,3,2-tet)Cl$_2$]$^+$ isomerizes to a mixture of *cis*- and *trans*-dichloro complexes in concentrated hydrochloric acid while *trans*-(*RS*)-[Co(2,3,2-tet)Cl$_2$]$^+$ undergoes no structural change under the same conditions. Second, the *trans*-(*RR*,*SS*) racemate aquates in acidic solution considerably faster than the *trans*-(*RS*) isomer; and, moreover, aquation in the former case proceeds with quantitative production of *cis*-chloroaquo complexes initially, while in the latter case the *trans* structure is retained. These observations not only substantiate that

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(2) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc.*, *Sect. A*, 1331 (1966).

(3) H. G. Hamilton, Jr., and M. D. Alexander, *Inorg. Chem.*, 5, 2060 (1966).

(4) The projections are in a plane perpendicular to the C$_2$ axis in the *RR* and *SS* cases and perpendicular to the δ_v plane in the *RS*(*meso*) case. Secondary nitrogen atoms, represented by dots, eclipse the primary nitrogen atoms, represented by circles. For an explanation of the *R*, *S* symbolism, see R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem. Intern. Ed. Engl.*, 5, 385 (1966).

(5) It should be pointed out that the *trans*-[Co(2,3,2-tet)(H$_2$O)Cl]$^{2+}$ isomers are of a unique type in coordination chemistry for they differ only in the interrelationship between geometrical structure and ligand configuration.

(6) Spectra were obtained using nitromethane as the solvent to suppress solvolysis.

(7) Spectra were obtained using Nujol mulls.

(8) This complex is configurationally analogous to *trans*-[Co(trien)-Cl$_2$]ClO$_4$ (trien = triethylenetetramine) prepared by other investigators.[1]

the complexes are isomerically pure but also show that the *RR* and *SS* nitrogen configurations enhance formation of *cis* structures relative to the *RS* configuration. The chemical behavior of these *trans*-dichloro diastereomers provide a vivid as well as unique illustration of how greatly the configurations about asymmetric coordinated nitrogen can influence the stereochemistry of coordination compounds.[9]

(9) This work was supported in part by National Science Foundation Grant No. GP-6813.

(10) National Science Foundation Summer Teaching Fellow, 1966; NASA Trainee, 1966–1967.

Hobart G. Hamilton, Jr.,[10] M. Dale Alexander
Chemistry Department, New Mexico State University
Las Cruces, New Mexico 88001

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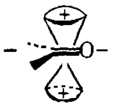
Structure by Nuclear Magnetic Resonance. XIV. On the Anisotropic Effects of the Carbonyl Group

Sir:

It is commonly accepted that a nucleus in conical regions extending above and below the plane of the carbonyl group is shielded; in the plane, it is deshielded (model I).[1] By using the recently published values of



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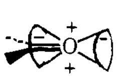
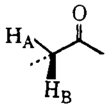


II

the three principal magnetic susceptibilities of the carbonyl bond,[2] model II can be constructed. The frequent use of model I in the elucidation of structural and conformational problems prompts us to report on the relative merits of I and II.

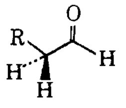
Model I predicts that H_A (III), in the plane of the carbonyl, will resonate at lower magnetic fields than H_B. Model II predicts the reverse, as seen from the



III

calculated screening constants,[3] σ, that are summarized in Table.

Table II summarizes chemical shifts, accurate to ±0.017 ppm, of some aldehydes and ketones. It was established[5] that the ratios IV/V and VI/VII decrease as R changes from methyl to ethyl to *t*-butyl. The corresponding upfield shift of the resonance of the α-protons caused by this change can be accommodated if H_A resonates at higher magnetic fields than H_B. Qualitatively, therefore, the experimental results agree with model II, not I. Quantitative agreement, however, between experimental and calculated chemical shifts (Table III) is poor.



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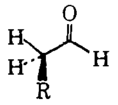

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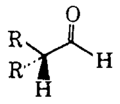

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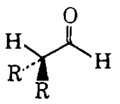
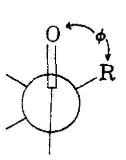


VII

Table I. Calculated Screening Constants, σ (in parts per million), for



R	ϕ, deg	$\sigma_{Ho} \times 10^6$	$\sigma_{Hm} \times 10^6$	$\sigma_E \times 10^6$
H_A	0	−0.19	+0.18	−0.63
H	60	−0.28		
H	90	−0.43	−0.22	−0.48
H_B	120	−0.50	−0.46	−0.43
H	180	−0.59	−0.70	−0.34
CH_3	0	+0.10		
CH_3	90	−0.11		
CH_3	131	−0.28		
CH_3	180	−0.38		

Table II. Chemical Shifts (in parts per million) of Aldehydes and Ketones in Dilute CCl_4

	$\delta(\alpha\text{-}CH_3)$	$\delta(\alpha\text{-}CH_2)$	$\delta(\alpha\text{-}CH)$
$MeCH_2CHO$		2.40	
$EtCH_2CHO$		2.33	
$t\text{-}BuCH_2CHO$		2.17	
$(Me)_2CHCHO$			2.40
$(Et)_2CHCHO$			1.93
$(t\text{-}Bu)_2CHCHO$			1.71
$MeCH_2COCH_3$	2.04	2.35	
$t\text{-}BuCH_2COCH_3$	1.98	2.19	
$(Me)_2CHCOCH_3$	2.04		2.50
$(Me)_2CHCOCH(Me)_2$			2.70
$(Me)_2CHCOC(Me)_3$			3.05

Table III. Experimental and Calculated $\Delta\delta$ (in parts per million) for α-Protons of RR′CHCHO

R	R′	$\Delta\delta$, exptl[a]	$\Delta\delta$, calcd[b]	$\Delta\delta$, calcd[c]
Me[d]	H	0.00	0.00	0.00
Et	H	0.067	0.017	0.025
t-Bu	H	0.23	0.070	0.10
Me[d]	Me	0.00	0.00	0.00
Et	Et	0.47	0.047	0.073
t-Bu	*t*-Bu	0.69	0.21	0.31

[a] From relative rotamer populations.[4] [b] From magnetic anisotropy with the magnetic dipole on the oxygen.[2] [c] From the sum of magnetic anistropy[2] and electric field,[4] by placing the dipoles at the center of the carbonyl bond. [d] Standard.

A most dramatic demonstration that H_A resonates at higher magnetic fields[6] than H_B is shown in Figure 1.

Further evidence that II, or a similar model, might be more realistic to use than I is the observation that in

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(1) See L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, Chapter 7, p 124.

(2) J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, A. K. G. Nasser, L. Saunders, and W. B. Whalley, *Chem. Commun.*, 754 (1966).

(3) Negative σ denotes deshielding and positive σ shielding. σ_{Ho} is the magnetic anisotropy screening calculated from the anisotropies of ref 2, and by placing the magnetic dipole on the oxygen atom; σ_{Hm} is that by placing the dipole at the midpoint of the carbonyl. σ_E is the electric field shielding calculated by using published data,[2,4] with the dipole at the mipoint of the carbonyl bond.

(4) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

(5) G. J. Karabatsos and N. Hsi, *J. Am. Chem. Soc.*, **87**, 2864 (1965).

(6) Rotamer populations were calculated from the dependence of J_{HH} on temperature and solvent, as in ref 5. Details of the work on dichloroacetaldehyde and bromoacetaldehyde will appear in a full paper.