

radical transfer process, although rare, are found in the reactions of alkylcobalt derivatives (such as alkylbis(dimethylglyoximate)cobalt) with  $\text{Cr}^{2+}$ <sup>14</sup> and  $\text{Co(II)}$  complexes.<sup>15</sup> The mechanism can be described<sup>14,16</sup> as an  $\text{SH}_2$  process at the saturated carbon center, or as an inner-sphere redox process involving a bridging ligand without an unshared electron pair.

There is probably little reason to doubt that homolysis (eq 1) and not heterolysis provides the initial step in the sequence comprising the overall decomposition of I. On the other hand, the interpretation of the kinetic data for decomposition in terms of the rate constant values given is subject to the two difficulties mentioned here. Moreover, serious internal inconsistency exists in that the steady-state assumption for [II] and  $[\text{Cr}^{2+}]$  made in interpreting<sup>2</sup> the half-order dependence of the decomposition rate on [I] (in the absence of added  $\text{Cr}^{2+}$ ) is inconsistent with the rate constant values given. Whatever the mechanism for the decomposition (and we are unable to suggest an explanation satisfying all the earlier observations<sup>2</sup> in themselves or to reconcile them with the new results), it is clear that chromium exchange occurs primarily by the direct pathway represented by reaction 8, which provides a better mechanism for exchange than the intramolecular homolytic dissociation step of reaction 1.

(14) (a) J. H. Espenson and J. S. Shveima, *J. Amer. Chem. Soc.*, **95**, 4468 (1971); (b) J. H. Espenson and T. D. Sellers, *ibid.*, **96**, 94 (1974).

(15) A. van den Bergen and B. O. West, *Chem. Commun.*, 52 (1971).

(16) D. Dodd and M. D. Johnson, *J. Organometal. Chem.*, **52**, 1 (1973).

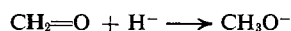
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Received November 10, 1973

### An *ab Initio* Study of Nucleophilic Addition to a Carbonyl Group<sup>1</sup>

Sir:

Nucleophilic additions to a carbonyl group leading to tetrahedral species which are products or intermediates in a mechanistic sequence occupy a central place in biochemistry as well as in organic chemistry. It has been shown recently<sup>1a</sup> that the structural pathway for the nucleophilic addition of an amino group to carbonyl can be mapped on the basis of crystal structure data. However, from structural data alone no direct information about the energy variation along the reaction pathway can be obtained. Furthermore, it was not entirely clear to what extent steric requirements of substituents on the nucleophile and the carbonyl group, as well as crystal packing effects, influence the arrangement of the reactive centers. In an attempt to fill these gaps we have carried out SCF-LCGO-MO calculations on the reaction path of the simple model system



corresponding to nucleophilic addition of hydride anion to formaldehyde to produce methanolate anion. A calculation has also been made for the system con-

(1) (a) Chemical Reaction Paths, Part III; for Part II see H. Bürgi, J. D. Dunitz, and E. Shefter, *J. Amer. Chem. Soc.*, **95**, 5065 (1973). (b) Theoretical Studies of Chemical Transformations Part II; for Part I see J. M. Lehn and G. Wipff, *J. Chem. Soc., Chem. Commun.*, 747 (1973).

sisting of an ammonia and a formaldehyde molecule at a separation of 2.0 Å.

The computations made use of an sp basis set of Gaussian-type functions. First the total energies of educt and product were minimized with respect to the structural parameters.<sup>2,3</sup> Then the intermediate stages of the reaction were studied at various distances  $d(\text{H}^- \cdots \text{C})$ . Assuming  $C_s$ -symmetry leaves five variables chosen as  $\alpha(\text{H}^- \cdots \text{CO})$ ,  $r(\text{C}-\text{O})$ ,  $r(\text{C}-\text{H}_1)$ ,  $\gamma(\text{H}_1\text{CH}_2)$ , and  $\Delta$  (the deviation of C out of the plane defined by  $\text{H}_1$ ,  $\text{H}_2$ , and O) which were optimized separately. Results are summarized in Table I and Figure 1.

Table I. Structural Parameters (See Text) and Total Energies for the  $\text{H}^- + \text{H}_2\text{CO}$  Reaction

	$d(\text{H}^- \cdots \text{C}),$ Å	$\alpha(\text{H}^- \cdots \text{CO}),$ deg	$\Delta,$ Å	$r(\text{CO}),$ Å	$E,$ au
	$\infty$		0.00	1.203	-114.0334
A	3.0	180	0.00	1.22	-144.0643
B	2.5	126	0.03	1.23	-114.0672
C	2.0	119	0.13	1.25	-114.0760
D	1.5	118	0.26	1.31	-114.0970
E	1.12	109.5	0.40	1.405	-114.1106

If the reaction between formaldehyde and  $\text{H}^-$  is accepted as a model for other reactions involving nucleophilic addition to  $\text{sp}^2$ -hybridized carbon, e.g., ester or amide formation and hydrolysis, our results bear relation to some of the concepts which have been developed for discussing such reactions: togetherness, proximity, orbital steering, orbital orientaton.<sup>4-7</sup>

The anion  $\text{H}^-$  approaches the formaldehyde molecule along the  $\text{H}_1\text{CH}_2$  bisector until  $d(\text{H}^- \cdots \text{C})$  is about 3 Å. Then the  $\text{H}^- \cdots \text{C}-\text{O}$  angle decreases from 180 to 125° while the distance  $\text{H}^- \cdots \text{H}_1$  and the energy of the system change only little and formaldehyde stays essentially planar. Finally  $\text{H}^-$  approaches carbon to within bonding distance, C becomes tetrahedrally coordinated, and the energy drops rapidly. This behavior may also be viewed as an initial freezing in of translational freedom, followed by a region of high amplitude librational freedom which then gradually transforms into internal vibrations of the methanolate anion. The potential energy valley becomes ever steeper and narrower as  $\text{H}^-$  approaches to within bonding distance of the carbon atom (Figure 1). Orbital interactions become important at distances shorter than 2.5 Å and determine more and more strongly the direction of approach. The first excited  $A_2$  state obtained from an  $n \rightarrow \pi^*$  electronic transition is non-

(2) The basis set of Gaussian functions consisted of seven s and three p functions on C, N, and O and of four s on H, contracted into three s, two p, and two s, respectively (7,3/4-3,2/2).<sup>3</sup> The calculated geometry of formaldehyde was in very good agreement with the experimental one.

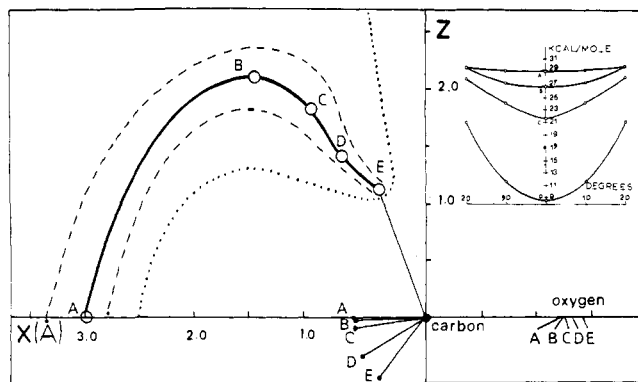
(3) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **17**, 209 (1970); A. Veillard IBMOL Version 4, Special IBM Technical Report, San Jose, Calif. (1968).

(4) D. R. Storm and D. E. Koshland, Jr., *J. Amer. Chem. Soc.*, **94**, 5815 (1972); A. Dafforn and D. E. Koshland, Jr., *Biochem. Biophys. Res. Commun.*, **52**, 779 (1973), and references therein.

(5) W. P. Jencks and M. I. Page, *Proceedings of the 8th Meeting of the Federation of European Biochemical Societies*, Amsterdam (1972), and references therein; M. I. Page and W. P. Jencks, *Proc. Nat. Acad. Sci. U. S. A.*, **68**, 1678 (1971).

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**Figure 1.** Minimum energy path for the  $\text{H}^- + \text{CH}_2\text{O}$  reaction (in the  $xz$  plane). The points A, B, C, D, and E correspond respectively to an  $\text{H}^- \cdots \text{C}$  distance of 3.0, 2.5, 2.0, 1.5, and 1.12 Å (see Table I). Energy curves for deviations of 0.6 (---) and 6.0 (....) kcal/mol from the minimum energy path are also shown. Insert top right: Energy profiles for lateral angular displacements (in degrees) out of the  $xz$  plane, at values of the  $x$  coordinate corresponding to points A, B, C, and D respectively. These profiles illustrate the more and more stringent "orientation" constraint of the  $\text{H}^-$  approach as the reaction proceeds. Energies are given in kcal/mol with respect to the energy of the most stable species (*i.e.*, point E, methanolate) taken as zero.

planar,<sup>8</sup> and correspondingly the gradual deviation from planarity of the formaldehyde molecule as the reaction proceeds can be attributed partly to the mixing of  $\pi^*$  with  $1s(\text{H}^-)$ , in agreement with the electron distribution calculated for the HOMO.

When  $\Delta$  (out-of-plane deformation) is plotted against  $d(\text{H}^- \cdots \text{C})$ , the resulting curve is strikingly similar to that obtained from the crystal structure data for the approach of an amino group to carbonyl. The points at 1.12, 1.5, and 2 Å follow a logarithmic relationship (Figure 2)

$$d(\text{H}^- \cdots \text{C}) = -1.805 \log + 0.415 \text{ \AA}$$

similar to the one found from structural data<sup>1a</sup>

$$d(\text{N} \cdots \text{C}) = -1.701 \log + 0.867 \text{ \AA}$$

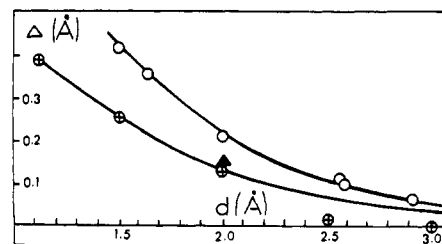
The difference in the constant term largely reflects the difference between the C-H and C-N bond lengths.

In order to compare the results derived from crystal structure data and model calculations, the energy of the species formaldehyde ammonia was minimized at a fixed  $\text{N} \cdots \text{C}$  distance of 2.0 Å. Calculated data are  $\Delta_{\text{corr}} = 0.14 \text{ \AA}$ ,<sup>9</sup>  $\alpha(\text{N} \cdots \text{C}-\text{O}) = 105^\circ$ , and  $r(\text{C}-\text{O}) = 1.23 \text{ \AA}$ . The experimental values at  $d(\text{N} \cdots \text{C}) = 1.993 \text{ \AA}$  are  $\Delta = 0.21 \text{ \AA}$ ,  $\alpha(\text{N} \cdots \text{C}-\text{O}) = 107 \pm 5^\circ$ , and  $r(\text{C}-\text{O}) = 1.258 \text{ \AA}$ .<sup>1a</sup>

Thus, although the angles of approach agree, the distortion of the carbonyl group observed in the crystal is larger than that calculated. This discrepancy could result from the differing microenvironments: polar in the crystal and therefore stabilizing the species  $\text{H}_3\text{N}^{\delta+} \cdots \text{H}_2\text{CO}^{\delta-}$  showing partial separation of charge, but nonpolar for isolated reactants considered in the calculation. Also, steric interactions—between alkyl sub-

(8) V. A. Job, V. Sethuraman and K. K. Innes, *J. Mol. Spectrosc.*, **30**, 365 (1969); V. T. Jones and J. B. Coon, *ibid.*, **31**, 137 (1969).

(9) In order to compare the value of  $\Delta$  calculated in this study (0.11 Å) with the experimental result, a correction has to be made for the difference between the C-C bond length in a ketone (1.53 Å from the experimental data<sup>1a</sup>) and the C-H bond length in formaldehyde (1.12 Å in this model calculation), yielding  $\Delta_{\text{corr}} = 0.14 \text{ \AA}$ .



**Figure 2.** Plot of the deviation  $\Delta$  of the C atom out of the  $\text{H}_1$ ,  $\text{H}_2$ , and O plane vs. the distance  $d$  between  $\text{H}^-$  and C of  $\text{H}_2\text{CO}$  (bottom curve) and between N and C of a carbonyl group as obtained experimentally from crystal structure data<sup>1a</sup> (top curve). The point  $\blacktriangle$  is that calculated for  $\text{NH}_3 + \text{H}_2\text{CO}$  at 2.0 Å  $\text{N} \cdots \text{C}$  separation and corrected to make it comparable to the structural data.<sup>9</sup>

stituents on the amino and carbonyl group of the real molecule<sup>1a</sup>—are reduced in the model system bearing hydrogen substituents only.

The qualitative agreement between the results calculated for isolated reactants and those derived from solid-state data encourages us to believe that the two descriptions complement and mutually confirm each other. Theoretical and experimental studies on other systems now in progress will provide further tests of our present results.

**Acknowledgments.** We thank the CNRS Computing Center of Strasbourg for providing the computer time used in this work. We also thank Professor J. D. Dunitz (ETH, Zurich) for his comments in the course of this study.

(10) This work was performed during a stay of H. B. Bürgi at the Institut de Chimie in Strasbourg.

(11) ERA No. 265 du CNRS.

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Received October 18, 1973

## Facile Carbon $\rightarrow$ Nitrogen and Nitrogen $\rightarrow$ Carbon Acyl Migrations in Acyl Derivatives of 2-Mercaptobenzimidazole. A Model of Biotin

Sir:

We wish to report a new type of acyl migration that should provide information useful in mechanistic studies of bioorganic or enzymic reactions. Migrations of acyl groups constitute an important class of reactions in biochemistry. Detailed studies, however, have been reported only for acyl migrations from one heteroatom to another, such as solvolyses of esters or amides. Yet, acyl migrations between carbon atoms and heteroatoms are also important in bioorganic reactions, *e.g.*, syntheses and degradations of fatty acids. These summarized in Scheme I are the first examples of acyl migrations between formally neutral carbon and formally neutral nitrogen under mild conditions.

When 2-benzimidazolyl disulfide (1) was treated at room temperature with benzoylacetone in the presence of sodium hydride,<sup>1</sup> 1-phenyl-2-(2'-mercaptobenzimid-

(1) T. Fujisawa, K. Hata, and T. Kojima, *Chem. Lett.*, 287 (1973).