levels of **3** in going to tropone (**1**) are the inductive effect of a carbonyl group (I_t) and the π_{CC},π_{CO} interaction (R_1), we obtain

$$\epsilon(b_1) = -7.80 + I_1 + R_1 = -8.90$$

$$\epsilon(a_2) = -9.57 + I_2 = -10.67 \qquad (3)$$

$$\epsilon(b_1) = -11.51 + I_3 + R_3 \leq -11.54$$

In this treatment we consider the inductive effect to be a perturbation of the Coulomb integrals of the terminal atoms of the triene only. More sophisticated treatments would consider the perturbations at all atoms; however, they are much smaller than the perturbations at the terminal atoms[14] and the gross assumptions of the above model do not justify their inclusion. Symmetry precludes any resonance interaction between the $a_2(\pi_{CC})$ level and the $b_1(\pi_{CO})$ level in **1**, hence $I_2 = -1.10$ eV. If

$$I_t = 2C_{t2}{}^2I_0 \qquad (4)$$

and $C_{12}{}^2 = 0.271$, $C_{22}{}^2 = 0.175$, and $C_{32}{}^2 = 0.054$,[15] then

$$I_0 = -3.14 \text{ eV} \qquad (5)$$

and

$$I_1 = -1.70 \text{ and } I_3 = -0.34 \text{ eV}$$

$$R_t = -\frac{(C_{t2}C_{CO}{}^\beta + C_{t7}C_{CO}{}^\beta)^2}{\epsilon(\pi_i) - \epsilon(\pi_{CO})}$$

$$= -\frac{C_{t2}{}^2}{\epsilon(\pi_i) - \epsilon(\pi_{CO})}4C_{CO}{}^2\beta^2 \qquad (6)$$

The energy of π_{CO} is not known with certainty, but it has been estimated at 13.5 eV.[16] Then, if $C_{CO} \simeq 1/\sqrt{2}$, $R_1 = +0.60$ eV and $|\beta| = 2.6$ eV and $R_3 = +0.31$ eV and $|\beta| = 3.1$ eV. The values of $|\beta|$ are in reasonable agreement considering all of the approximations used. A similar correlation diagram and calculation can be obtained starting with cis-1,3,5-hexatriene.[11]

Using the above values of I_0, an average value for $|\beta|$, eq 4 and 6, and $\pi_{CC}{}^0 = -9.18$ eV,[17] to calculate the πIP of 2-cyclopentenone, one gets

$$\epsilon(\pi_{CC}) = \pi_{CC}{}^0 + I + R$$

$$= -9.18 - 1.57 + 0.47 = -10.28$$

to be compared with the measured value of 10.10 eV.[3] We have not included any contribution for the inductive effect of the carbonyl group transmitted to C-3 of 2-cyclopentenone via the saturated carbons.[18]

This calculated inductive parameter, eq 5, only applies to α,β-unsaturated ketones and it actually contains both the inductive effect and the change in σ,π interactions $R_t{}^{\sigma,\pi}$.[18] In fact, from CNDO/2 calculations on **1**, **2**, **3**, and heptafulvalene (**4**), it appears that

4
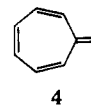
the inductive effect of the oxygen atom in **1** is small when comparing **1** and **4** as suggested earlier.[3]

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Bimolecular Alkyl Transfer between Chromium(II) and the 4-Pyridinomethylchromium(III) Cation

Sir:

The thermal decomposition of 4-pyridinomethylchromium(III) ion, I, was proposed to proceed by an initial homolytic dissociation (eq 1) in aqueous per-

$$Cr_{aq}{}^{2+} + \cdot CH_2 - \langle\bigcirc\rangle NH^+ \qquad (k_1, k_{-1}) \quad (1)$$

II
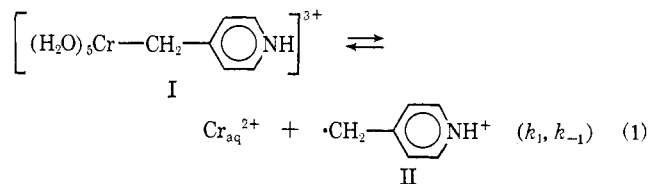
chloric acid solutions under aerobic conditions.[1] Studies of Schmidt and Swaddle[2] lent support to the same reaction under anaerobic conditions.

We undertook to examine further aspects of this purported homolysis through a study of (a) the rate of exchange of chromium atoms between I and $^{51}Cr_{aq}{}^{2+}$, for which reaction 1 would provide a pathway and (b) the rate of radical recombination, k_{-1} of eq 1.

The present studies were carried out under the same conditions used in the earlier work,[1,2] 55° and 1.00 F HClO₄. Solutions of I were prepared and purified as before,[1,2] and the exchange initiated by addition of ^{51}Cr-tagged Cr^{2+} in a rigorously oxygen-free environment. Samples were withdrawn by syringe at appropriate intervals, and quenched by oxidation of Cr^{2+}.[3-5] For each experiment a plot was constructed of log (1 − fraction exchange) vs. time according to the McKay equation,[6] permitting computation of the ex-

(14) J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory," 2nd ed, Wiley, London, 1970, Chapter 16.

(15) The C_{t2} are the coefficients of π_i at carbon 2 (and 7) from the simple Hückel treatment of cycloheptatriene (**2**). Note the numbering system to correlate with **1**.

(16) C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Amer. Chem. Soc.*, **94**, 1451 (1972).

(17) P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970).

(18) This point will be dealt with in subsequent papers.

(1) (a) R. G. Coombes, M. D. Johnson, and N. Winterton, *J. Chem. Soc.*, 7029 (1965); (b) R. G. Coombes and M. D. Johnson, *J. Chem. Soc. A*, 177 (1966).

(2) A. R. Schmidt and T. W. Swaddle, *J. Chem. Soc. A*, 1927 (1970).

(3) A convenient oxidizing agent was [Co(NH₃)₅Br]Br₂, although in early experiments oxygen was used with comparable results.

(4) The procedure consisted of chromatography of each sample on a 7-cm column of Dowex 50W-X2 cation exchange resin, eluting I with 2 F HClO₄. The purest and most concentrated fractions of I were combined and oxidized to chromate with alkaline peroxide. In this form the specific activity of I was determined from the measured Cr-51 activity and the spectrophotometric analysis as chromate.

(5) A sample was withdrawn early and late in each run to analyze for [Cr²⁺]; this served to measure the exact concentration of Cr²⁺ present, and its constancy confirmed the absence of net reactions which consume Cr²⁺.

(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd ed, McGraw-Hill, New York, N. Y., 1961, pp 192–193.

change rate according to

$$R_{ex} = \frac{\ln 2}{t_{1/2}} \frac{[Cr^{2+}][I]}{[Cr^{2+}] + [I]} \qquad (2)$$

A series of such experiments with different concentrations of I and of $[Cr^{2+}]$ served to establish the rate expression

$$R_{ex} = k_{ex}[I][Cr^{2+}] \qquad (3)$$

with $k_{ex} = 5.8 \pm 0.5 \times 10^{-2}\ M^{-1}\ sec^{-1}$ (55°, 1.00 F $HClO_4$). The first-order dependence upon $[Cr^{2+}]$ is an important point, which is illustrated in Figure 1 by the linear plot of $R_{ex}/[I]$ vs. $[Cr^{2+}]$. The figure also shows the expected value of the Cr^{2+}-independent pathway for exchange based on the reported value[2] of $k_1 = 5.2 \times 10^{-5}\ sec^{-1}$ (55°, 1 F $HClO_4$), derived from the interpretation of the kinetic study of the decomposition process. Equilibration of I with unlabeled Cr^{2+} prior to addition of the tag was without effect. The main pathway for exchange is thus the bimolecular reaction of I with Cr_{aq}^{2+}; homolytic dissociation constitutes at best a minor pathway for exchange. Parallel bimolecular and unimolecular exchange can be considered as in mercury exchange between Hg(II) and pyridinomethylmercuric salts,[7] but the intercept of nearly zero in Figure 1 indicates that the unimolecular pathway, if it does exist,[8] occurs at a specific rate much below $5.2 \times 10^{-5}\ sec^{-1}$.

The second set of measurements concerns the rate of the reaction between the alkyl bromide (III) and Cr^{2+}, which is the reaction used[1,2] for synthesizing I.

$$BrCH_2-\underset{III}{\underline{\langle\bigcirc\rangle}}NH^+ + 2Cr_{aq}^{2+} = CrBr^{2+} + I \qquad (4)$$
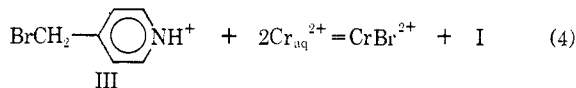
The following two-step mechanism, in which the first step is much slower than the second, is accepted for such reactions of Cr^{2+} [1,9] as well as for analogous reactions of Co(II).[10]

$$III + Cr_{aq}^{2+} \longrightarrow II + CrBr^{2+} \qquad (k_5) \qquad (5)$$

$$II + Cr_{aq}^{2+} \longrightarrow I \qquad (k_{-1}) \qquad (6)$$
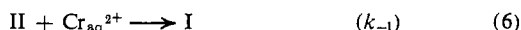
Rate measurements were carried out on the rate of reaction 4 over a wide range of concentrations (1.3×10^{-5} to $6.8 \times 10^{-3}\ M$ III, 3×10^{-5} to $4.0 \times 10^{-3}\ M$ Cr^{2+}), including experiments where each reactant is in excess. The kinetic data are in excellent accord with the expression

$$-d[III]/dt = k_5[III][Cr^{2+}] \qquad (7)$$

with k_5 (55.0°) = $16.9 \pm 0.7\ M^{-1}\ sec^{-1}$ in 1.0 F $HClO_4$ and 12.9 ± 0.6 in 0.10 F $HClO_4$. In addition the yield of I in each run was estimated spectrophotometrically from the intensity of the absorption peak at λ 308 nm (ϵ 1.6 $\times$ $10^4\ M^{-1}\ cm^{-1}$). Quantitative yields were
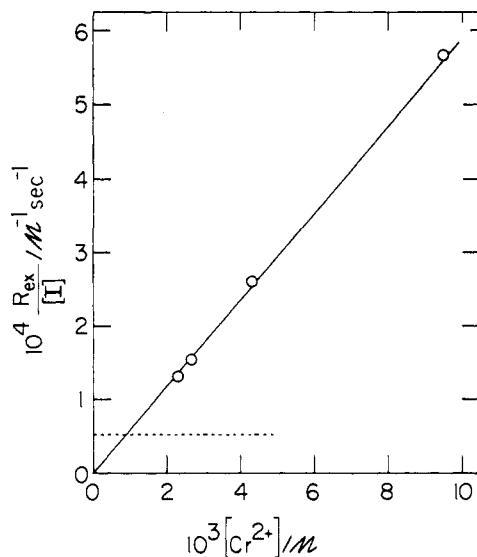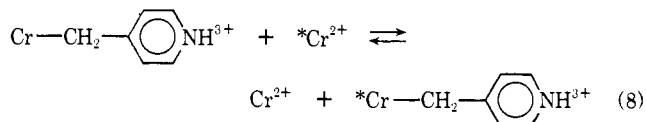

Figure 1. A plot illustrating the first-order dependence of the rate of chromium exchange upon $[Cr^{2+}]$. The horizontal dashed line represents the predicted behavior were reaction 1, at the specific rate reported, providing the only pathway for chromium exchange.

obtained in experiments with excess Cr^{2+}, as expected. With limiting $[Cr^{2+}]$, however, yields between 30 and 55% of theoretical were found, presumably because the dimerization of radical II competes with reaction 6 at low $[Cr^{2+}]$.

Based on analysis of the kinetics data, particularly the agreement of k_5 determined under both sets of concentration conditions, a lower limit on $k_{-1} > 10^3\ M^{-1}$ sec^{-1} can be set.[11] Considering also the yield data a rough estimate of $k_{-1} \sim 10^{5.8}\ M^{-1}\ sec^{-1}$ can be made.[12] This is inconsistent with the indirectly determined value, $k_{-1} = 10^{-2}\ M^{-1}\ sec^{-1}$ (55°, 0.03 F $HClO_4$), of Schmidt and Swaddle.[2] We note, however, that in related reactions of Cr^{2+} and organic radicals generated by pulse radiolysis,[13] rate constants analogous to k_{-1} of $10^6 - 10^8$ $M^{-1}\ sec^{-1}$ were found, indicating the reasonableness of the estimate of k_{-1} made here.

The kinetic data suggest the exchange reaction occurs via a bimolecular mechanism. Precedents for this

$$Cr-CH_2-\langle\bigcirc\rangle NH^{3+} + {}^*Cr^{2+} \rightleftarrows$$

$$Cr^{2+} + {}^*Cr-CH_2-\langle\bigcirc\rangle NH^{3+} \qquad (8)$$

(7) D. Dodd, C. K. Ingold, and M. D. Johnson, J. Chem. Soc. B, 1076 (1969).

(8) Were the exchange proceeding by the parallel pathway mechanism, the plot of $R_{ex}/[I]$ vs. $[Cr^{2+}]$ would be linear over the entire range of $[Cr^{2+}]$ having as intercept the value of k_1.

(9) (a) D. Dodd and M. D. Johnson, J. Chem. Soc. A, 34 (1968); (b) C. E. Castro and W. C. Kray, J. Amer. Chem. Soc., 88, 4447 (1966); (c) J. K. Kochi and D. D. Davis, ibid., 86, 5264 (1964).

(10) (a) P. W. Schneider, P. F. Phelan, and J. Halpern, J. Amer. Chem. Soc., 91, 77 (1969); (b) J. Halpern and P. F. Phelan, ibid., 94, 1881 (1972); (c) J. Halpern and J. P. Maher, ibid., 86, 2311 (1972); 87, 5361 (1965).

(11) The Runge-Kutta method was used to solve the differential rate equations associated with reactions 5 and 6 without making the steady-state approximation for [II]. With k_5 held at the experimental value, computations were carried out using different values of k_{-1}. A value of $k_{-1} > 10^3\ M^{-1}\ sec^{-1}$ was consistent with the observed rate law and the constancy of k_5 within the indicated limits with either III or Cr^{2+} in excess.

(12) The yield of I permits the estimate of k_{-1} from the expression

$$k_{-1} = \left\{ \frac{k_5(2k_t)[III]Y^2}{[Cr^{2+}](1-Y)} \right\}^{1/2}$$

where $2k_t$ is the rate constant for dimerization of II, estimated as 10^9 $M^{-1}\ sec^{-1}$ (K. U. Ingold in "Free Radicals," J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, pp 40–56), and Y is the observed yield of I. In six experiments with limiting $[Cr^{2+}]$, the value of k_{-1} so calculated (using $[Cr^{2+}]$ at the midpoint of the run) were $10^{5.6} - 10^{6.2}\ M^{-1}\ sec^{-1}$. In view of the assumed values of $2k_t$, the use of an average $[Cr^{2+}]$, and the uncertainties associated with the very low $[Cr^{2+}]$, we regard this as an indication of the magnitude of k_{-1}, and not an accurate evaluation.

(13) H. Cohen and D. Meyerstein, J. Chem. Soc., Chem. Commun., 320 (1972).

radical transfer process, although rare, are found in the reactions of alkylcobalt derivatives (such as alkylbis-(dimethylglyoximato)cobalt) with Cr^{2+} [14] and Co(II) complexes.[15] The mechanism can be described[14,16] as an S_H2 process at the saturated carbon center, or as an innersphere 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 [Cr^{2+}] made in interpreting[2] the half-order dependence of the decomposition rate on [I] (in the absence of added 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[2] 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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An *ab Initio* Study of Nucleophilic Addition to a Carbonyl Group[1]

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[1a] 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

$$CH_2{=}O + H^- \longrightarrow CH_3O^-$$
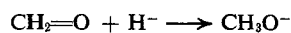
corresponding to nucleophilic addition of hydride anion to formaldehyde to produce methanolate anion. A calculation has also been made for the system con-

(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.[2,3] Then the intermediate stages of the reaction were studied at various distances $d(H^-\cdots C)$. Assuming C_s-symmetry leaves five variables chosen as $\alpha(H^-\cdots CO)$, $r(C{-}O)$, $r(C{-}H_1)$, γ (H_1CH_2), and Δ (the deviation of C out of the plane defined by H_1, 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 $H^- + H_2CO$ Reaction

	$d(H^-\cdots C)$, Å	$\alpha(H^-\cdots CO)$, deg	Δ, Å	$r(CO)$, Å	E, au
	∞		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 H^- is accepted as a model for other reactions involving nucleophilic addition to 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.[4–7]

The anion H^- approaches the formaldehyde molecule along the H_1CH_2 bisector until $d(H^-\cdots C)$ is about 3 Å. Then the $H^-\cdots C{-}O$ angle decreases from 180 to 125° while the distance $H^-\cdots H_1$ and the energy of the system change only little and formaldehyde stays essentially planar. Finally 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 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).[3] 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.*, **68**, 1678 (1971).
(6) P. Deslongchamps, C. Lebreux, and R. Taillefer, *Can. J. Chem.*, **51**, 1665 (1973), and references therein.
(7) C. S. Kim and L. L. Ingraham, *Biochim. Biophys. Acta*, **297**, 220 (1973).