TABLE I

RATE CONSTANTS FOR THE OXIDATION OF $(NH_3)_5Co\cdot OCHO^{2+}$ BY MnO_4^- (μ = 1.0)[a]

Temp., °C.	$[(NH_3)_5Co\cdot OCHO(ClO_4)_2] \times 10^3$, M	$[KMnO_4] \times 10^2$, M	$[HClO_4]$, M	$k \times 10^2$, M^{-1} sec.$^{-1}$	$\frac{[(NH_3)_5Co\cdot OH_2^{3+}]}{[Co^{2+}]}$
0.1	1.5	1.5	0.1	2.54	...
.1	1.5	4.8	.1	2.55	...
.1	6.0	4.8	.1	2.64	...
.1	3.0	1.0	.1	...	3.5 (3.5)[b]
.1	3.0	2.0	.1	...	6.6 (6.4)[b]
.1	3.0	4.0	.1	...	10.5 (11.2)[b]
.1	3.0	5.0	.1	2.55 (0.232)[b]	14.5
.1	3.0	10	.1	...	29 (25)[b]
.1	3.0	4.8	1.0	2.17	...
14.8	3.0	4.8	0.1	9.25	...
20.0	3.0	4.8	.1	14.5	...
25.0	3.0	4.8	.1	21.3	...

[a] Adjusted with $NaClO_4$. [b] Using $(NH_3)_5Co\cdot OCDO^{2+}$ in place of $(NH_3)_5Co\cdot OCHO^{2+}$

$$(NH_3)_5Co\cdot OCHO^{2+} + {}^2/_3MnO_4^- \longrightarrow CO_2 + (NH_3)_5Co\cdot OH_2^{3+} + {}^2/_3MnO_2$$

The ratio of unreduced to reduced cobalt was found to depend on the concentration of MnO_4^- according to

$$[(NH_3)_5Co\cdot OH_2^{3+}]/[Co^{2+}] = 3 \times 10^2\,[MnO_4^-] \quad (1)$$

3. Substitution of $(NH_3)_5Co\cdot OCDO^{2+}$ for $(NH_3)_5Co\cdot OCHO^{2+}$ reduced the rate by a factor of 10.5 but the stoichiometry of the reaction was substantially unchanged.

These observations provide strong support for the mechanism

$$[(NH_3)_5Co^{III}(OCHO^-)]^{2+} + MnO_4^- \xrightarrow{k} [(NH_3)_5Co^{III}(CO_2^-)]^{2+} + HMnO_4^-$$

$$[(NH_3)_5Co^{III}(CO_2^-)]^{2+} \xrightarrow{k_1} Co^{2+} + CO_2$$

$$[(NH_3)_5Co^{III}(CO_2^-)]^{2+} + MnO_4^- \xrightarrow{k_2} (NH_3)_5Co^{III}OH_2^{3+} + CO_2$$

in which Co^{2+} and $(NH_3)_5Co^{III}OH_2^{3+}$ arise through competitive reactions of a common intermediate of finite lifetime, formed by an initial rate-determining one-electron oxidation step. The large deuterium kinetic isotope effect and the observation that the reaction stoichiometry is unaffected by this isotopic substitution further suggest that this initial one-electron oxidation is effected by abstraction of an H atom. Equation 1 yields $k_2/k_1 = 3 \times 10^2\ M^{-1}$.

The permanganate oxidation of formic acid itself in aqueous solution has previously been found[4] to proceed according to the rate law

$$-d[HCOOH]/dt = k_{HCOOH}[HCOOH][MnO_4^-] + k_{HCOO^-}[HCOO^-][MnO_4^-]$$

corresponding to contributions from separate paths involving reactions of MnO_4^- with HCOOH and $HCOO^-$. In the light of the comparison revealed by Table II it is tempting to draw the conclusion that the oxidation of

TABLE II

COMPARISON OF KINETIC PARAMETERS

Reductant	$k_{25°}$, M^{-1} sec.$^{-1}$	ΔH^*, kcal./mole	ΔS^*, e.u.	k_{C-H}/k_{C-D}
$(NH_3)_5Co\cdot OCHO^{2+}$	0.21	13.3	−17	10.5
$HCOO^-$[a]	3.0	12.4	−15	7–10
HCOOH[a]	1.6×10^{-3}	15.8	−19	1.0

[a] Based on data in ref. 4.

$(NH_3)_5Co\cdot OCHO^{2+}$ and of free $HCOO^-$ proceed through similar mechanisms, *i.e.*, that the reaction of $HCOO^-$ with MnO_4^- also involves transfer of an H atom rather than, as previously suggested,[4,5] of an H^- ion. The recent suggestion of Stewart and Mocek[6] that the permanganate oxidation of various alkoxide ions may also involve H atom, rather than H^- ion, transfer is of interest in this connection.

(6) R. Stewart and M. M. Mocek, *Can. J. Chem.*, **41**, 1160 (1963).

Studies are in progress on the oxidation of $(NH_3)_5Co\cdot OCHO^{2+}$ by other oxidants. Preliminary results suggest that oxidation by Co_{aq}^{3+} produces $(NH_3)_5Co\cdot OH_2^{3+}$ in nearly quantitative yield. $(NH_3)_5Co\cdot OH_2^{3+}$ is also the major product of the Ag^+-catalyzed oxidation by $S_2O_8^-$.[7] These results contrast with the behavior previously reported for the corresponding oxalato and *p*-aldehydobenzoato complexes, both of which yield predominantly Co^{2+} with these oxidants. The significance of these unexpected differences is not altogether clear and is being further examined.

Acknowledgment.—This work was initiated at the University of British Columbia, Vancouver, Canada, with support from the National Research Council of Canada, and is being continued at the University of Chicago with support from the National Science Foundation through Grant GP 654.

(7) R. A. Palmer and J. Halpern, unpublished results.

(8) National Research Council of Canada Postdoctoral Fellow, University of British Columbia, 1961–1962.

(9) Alfred P. Sloan Research Fellow.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF CHICAGO
CHICAGO 37, ILLINOIS

JOHN P. CANDLIN[8]
JACK HALPERN[9]

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A Quantitative Test for a Classical Carbonium Ion Mechanism

Sir:

The mechanism given in Chart I has been proposed to explain the highly stereospecific nature of the open carbonium ion intermediates presumed to have been formed during deamination of (+)-1,2,2-triphenylethyl-1-C^{14}-amine (Ia).[1-3] We also have reported[4-7] the results of several stereospecific ketone-forming deaminations of amino alcohols which demand the presence of open carbonium ion intermediates. In spite of these facts,[3-7] however, there is still considerable reluctance to abandon the idea that open carbonium ions are essentially racemic intermediates.[8,9]

(1) C. J. Collins, W. A. Bonner, and C. T. Lester, *J. Am. Chem. Soc.*, **81**, 466 (1959).

(2) C. J. Collins, J. B. Christie, and V. F. Raaen, *ibid.*, **83**, 4267 (1961).

(3) See also: (a) S. Winstein and E. Grunwald, *ibid.*, **70**, 835 (1948); (b) S. Winstein and B. K. Morse, *ibid.*, **74**, 1134 (1952); (c) S. Winstein and L. L. Ingraham, *ibid.*, **77**, 1739 (1955).

(4) B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *ibid.*, **79**, 6160 (1957).

(5) B. M. Benjamin, P. Wilder, Jr., and C. J. Collins, *ibid.*, **83**, 3654 (1961).

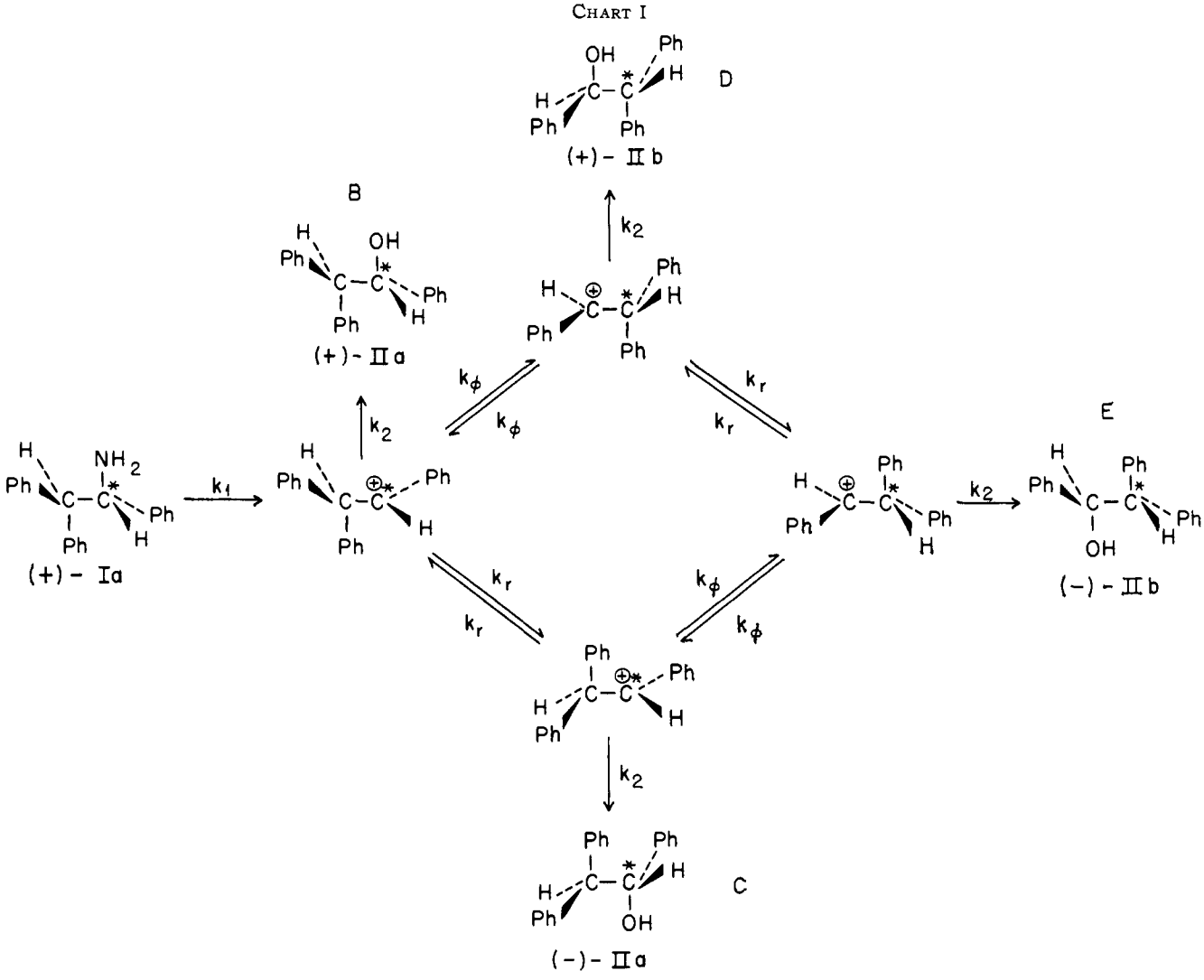
(6) B. M. Benjamin and C. J. Collins, *ibid.*, **83**, 3662 (1961).

(7) C. J. Collins, M. M. Staum, and B. M. Benjamin, *J. Org. Chem.*, **27**, 3525 (1962).

(8) P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963).

(9) W. Hückel and K. Heyder, *Chem. Ber.*, **96**, 220 (1963).

CHART I



The deamination of (+)-Ia cannot proceed solely through nonclassical phenonium ions[10] of either the *cis*- or *trans*-variety, or a combination of both, because the formation of inverted, unrearranged product [(−)-IIa], corresponding to path C in Chart I, then would not be possible. Nor can (−)-IIa be a consequence only of an SN2 attack[11] of hydroxyl, with the rest of the reaction proceeding through *cis*- and *trans*-phenonium ions, for then the moles of (+)-IIa minus the moles of (−)-IIb should equal the moles of (+)-IIb, a condition which has never been approximated in any of our previous[1,2] experiments. The question still remains, however, whether the observations of Collins, *et al.*,[1,2] are compatible with a mixed bridged–open carbonium ion mechanism.

In order to answer the foregoing question, we set up the rate expressions for formation and disappearance of all intermediate ions of Chart I, together with those for disappearance of reactant and formation of products. The expressions were integrated between the limits $t = 0$ and $t = \infty$, and using the Hearon area theorem,[12] the following four equations were derived where m_b–m_e are the mole fractions of product obtained through paths B–D, respectively. Employing these equations, data from three deaminations[1,2] were used to obtain the best values of k_2/k_ϕ and k_r/k_ϕ.[13]

TABLE I

COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF m_b, m_c, m_d, AND m_e USING EQ. 1–4 AND THE DATA OF REF. 1 AND 2

Run no.		Contribution of path B	C	D	E	$\frac{k_r}{k\phi}$	$\frac{k_2}{k\phi}$
1	Obsd.	0.556	0.215	0.144	0.085	1.76 ± 0.15[a]	2.26 ± 0.15
	Calcd.	.5530	.2124	.1424	.092		
2	Obsd.	.526	.212	.174	.088	1.28 ± .3	1.55 ± .2
	Calcd.	.5172	.2015	.1714	.1100		
3	Obsd.	.470	.253	.170	.110	1.89 ± .5	1.31 ± .3
	Calcd.	.4713	.2384	.1693	.1266		
4[b]	Obsd.	.496	.185	.199	.120	0.8875 ± .008	1.14 ± .006
	Calcd.	.4964	.1850	.1991	.1195		

[a] Standard error. [b] These data are the averages of several runs for the thermal decomposition of N-acetyl-N-nitroso-1,2,2-triphenylethyl-C^{14}-amine.

(10) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863, 3875 (1949); **74**, 2129, 2137 (1952).

(11) E. Renk and J. D. Roberts, *ibid.*, **83**, 878 (1961).

(12) B. M. Benjamin and C. J. Collins, *ibid.*, **78**, 4329 (1956).

(13) This was done using a linear least-squares program written for the I.B.M. 7090 computer by Dr. M. H. Lietzke.

$$(m_d - m_b) = \frac{k_2}{k_\phi}(m_b - 1) + \frac{k_r}{k_\phi}(m_b - m_c) \quad (1)$$

$$(m_e - m_c) = \frac{k_2}{k_\phi} m_c + \frac{k_r}{k_\phi}(m_c - m_d) \quad (2)$$

$$(m_b - m_d) = \frac{k_2}{k_\phi} m_d + \frac{k_r}{k_\phi}(m_d - m_e) \quad (3)$$

$$(m_c - m_e) = \frac{k_2}{k_\phi} m_e + \frac{k_r}{k_\phi}(m_e - m_d) \quad (4)$$

The extent of error in calculating these values is illustrated by using them to recalculate m_b–m_e from eq. 1–4. The observed and calculated mole fractions are in good agreement, and are listed in Table I (runs 1–3).

The same calculations were applied to the data obtained for the thermal decomposition of N-acetyl-N-nitroso-1,2,2-triphenylethylamine,[2] which has been postulated to go through the same intermediates. The results are given in Table I (run no. 4).

The results in Table I demonstrate the compatibility of the classical carbonium ion mechanism of Chart I with the data both for the deaminations[1,2] and for the thermal decomposition of N-acetyl-N-nitroso-1,2,2 triphenylethylamine. They also provide quantitative information concerning the relationship between k_2, k_ϕ, and k_r, which are shown to be of the same order of magnitude for the reactions studied. Equations 1–4 in addition permit us to calculate the extent of carbon[14] rearrangement and the amount of inversion for all possible values of k_2/k_ϕ and k_r/k_ϕ.

Acknowledgment.—We wish to acknowledge helpful discussions with Drs. M. H. Lietzke, R. W. Stoughton, and William Busing.

(14) Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

OAK RIDGE NATIONAL LABORATORY[14] CLAIR J. COLLINS
OAK RIDGE, TENNESSEE BEN M. BENJAMIN

RECEIVED APRIL 29, 1963

Kinetic Evidence for the Carbanion Mechanism of Dehydrohalogenation

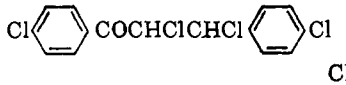
Sir:

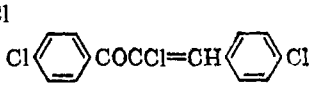
The two-step character of the E_1CB (carbanion) mechanism of certain base-catalyzed elimination reactions[1] should be disclosed not only by exchange[1c,d] and stereochemical[1e] evidence, but also by kinetics[1f] characteristic of the consecutive reactions 1 and 2.

$$SHX + B \underset{k_{-1}^B}{\overset{k_1^B}{\rightleftharpoons}} SX^- + BH^+ \quad (1)$$

$$SX^- \xrightarrow{k_2} S + X^- \quad (2)$$

We wish to report that the dehydrochlorination of *erythro*-4,4′-dichlorochalcone dichloride (I), studied in





I[2] *erythro* (m.p. 143.5°; max 262 mμ, ε 19,000)
II[2] *threo* (m.p. 97.5°; max 263 mμ, ε 18,000)
III[2] *trans* (m.p. 62°; max 310 mμ, ε 21,400)
IV[2] *cis* (m.p. 101°; max 262 mμ, ε 23,500)

(1) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 422–423; (b) J. F. Bunnett, *Angew Chem.*, **74**, 731 (1962); (c) L. C. Leitch and H. J. Bernstein, *Can. J. Res.*, **28B** 35 (1950); (d) P. S. Skell and C. R. Hauser, *J. Am. Chem. Soc.*, **67**, 1661 (1945); (e) S. J. Cristol, *ibid.*, **69**, 338 (1947); C. H. DuPuy, R. D. Thurn, and G. F. Morris, *ibid.*, **84**, 1315 (1962); (f) J. Hine, R. Weisboeck, and O. B. Ramsay, *ibid.*, **83**, 1222 (1961).

(2) These compounds gave the correct C and H analyses. III was first prepared by R. T. K., and I by C. O. Hugvins, unpublished results (with S. F. Clark), University of Mississippi.

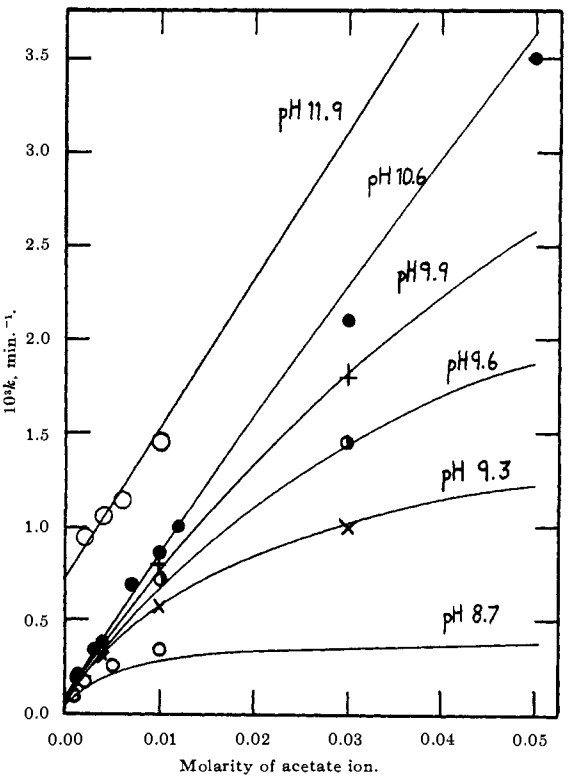


Fig. 1.—Family of curves (eq. 3) and experimental points showing pH dependence of the acetate-catalyzed elimination.

ethanolic acetate buffers, closely follows the rate equation[3] (3) for the above mechanism in the range where the steady-state method is applicable.

$$k = \frac{k_2 K_{SHX} \Sigma k_1^B [B]}{k_2 K_{SHX} + [H^+] \Sigma k_1^B [B]} \quad (3)$$

The most striking demonstration of conformity with eq. 3 is shown in Fig. 1. The *curves* are calculated, with $k_1^{EtOH} = 5 \times 10^{-5}$ min.$^{-1}$, $k_1^{EtO^-} = 1.08 \times 10^4$ l. mole^{-1} min.$^{-1}$, $k_1^{OAc^-} = 7.9 \times 10^{-2}$ l. mole^{-1} min.$^{-1}$, and $k_2 K_{SHX} = 9.1 \times 10^{-13}$. The ion product of ethanol is assumed to be 7.9×10^{-20}. The experimental points clearly show the required general base catalysis modified by the pH-dependent second term in the denominator of eq. 3. A high concentration either of buffer or of hydrogen ion will increase this term, so that k approaches $k_2 K_{SHX}/[H+]$ and the rate itself approaches $k_2[SX^-]$. This corresponds to a rate-controlling second step and under these conditions the curves of Fig. 1 level off as equilibrium is approached in the acid–base step (1).

Considering the uncertainties of pH measurement in absolute ethanol, the rates measured over a wider range of acidity are in satisfactory agreement with the calculated pH–rate profile (Fig. 2). The conditions used were: pH 5, hydrochloric or perchloric acid solutions (the dehydrohalogenation is practically halted at this acidity and is therefore self-decelerating when unbuffered[4]); pH 8–12, the acetate buffers of Fig. 1, extrapolated to zero concentration; pH 13, veronalate buffers; pH 15–16, sodium ethoxide.

On the lower part of the pH–rate profile, step 2 is rate-controlling. As the pH increases past 8, a plateau appears as the second term in the denominator of eq. 3 becomes small and the ionization (1) rate-controlling with B = EtOH. Ethoxide ion begins to contribute appreciably as the base B around pH 10, causing a steady

(3) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp. 134–135. Equation 3 is an expression of the more obvious form, $k = k_2 \Sigma k_1^B[B]/(k_2 + \Sigma k_{-1}^B[BH^+])$, in terms of fewer constants.

(4) R. T. Kemp, Dissertation, University of Virginia, 1959.