yield, b.p. 74–83° (0.3 mm.); $n^{20}D$ 1.5002; $\alpha^{25}D$ $-15°$. The irone mixture was shown by infrared and gas–liquid partition chromatography to consist of about 57% α-neoisoirone[8] (4-phenylsemicarbazone,[9] m.p. 174–175° from ethanol. (Found: C, 74.02; H, 8.43.)), 10.5% α-irone; 8.2% β-irone, 8.4% lights and 16% high boiling isomer (4-phenylsemicarbazone, m.p. 144° from ethanol (Found: C, 74.03; H, 8.18)). The structure of the latter isomer is being elucidated.

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(8) The structure of α-neoisoirone was established by Y. R. Naves and P. Ardizio, *Bull. Soc. Chim. France*, 1479 (1955).

(9) Pseudoirone from Hoffmann-La Roche, Inc.,[5] Nutley, N. J., gave upon cyclization with 85% phosphoric acid 16% α-irone, 10.5% β-irone, 7% lights, and 66.5% α-neoisoirone (4-phenylsemicarbazone, m.p. 174° from ethanol). Mixed melting point with 4-phenylsemicarbazone of α-neoisoirone from cyclobutirone, 174°. Both derivatives show identical infrared spectra in KBr pellets.

THE GIVAUDAN CORPORATION
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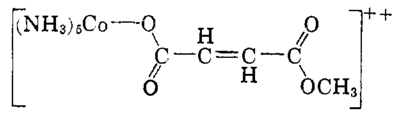
RECEIVED APRIL 1, 1959

SUBSTITUTION COUPLED TO ELECTRON TRANSFER[1]

Sir:

Rate comparisons[2] made for a series of pentamminecobaltic complexes reacting with Cr^{++} aq. suggest that when appropriate bridging groups are associated with Co(III), electron transfer takes place by remote attack of Cr^{++}, the electron flowing through the bond system of the bridging group. The results reported now seem to constitute definite proof for this conclusion.

The ion



(to be subsequently represented as $RFCH_3^{++}$) reacts with Cr^{++}aq. at almost the same rate as does the corresponding complex with fumaric acid in place of the half-ester. In both systems, good stoichiometry for the oxidation–reduction process is observed, one Co^{++}aq. (and $5NH_4^+$) being formed for each Cr^{++}aq. which reacts.

Now it should be noted that remote attack by Cr^{++}aq. on the half-ester will leave both Cr(III) and CH_3 attached to the remote carboxyl. The resulting structure would not be stable, so that ester hydrolysis may be expected to ensue on electron transfer. We cite evidence that this reaction does indeed take place. When Cr^{++}aq. in equivalent amount is added to 0.01 *M* $RFCH_3^{++}$ in the presence of 0.1 *M* $HClO_4$, and the solution immediately after reaction is titrated to *p*H 4.5 with standard alkali, we observe that acid has been produced equivalent in amount to the complex which has reacted. When such mixtures after reaction are distilled at 4°, variable amounts of CH_3OH are detected in the distillate, but comprising only 2 to 7% of the total CH_3OH. In a blank experiment, similar in every respect except that Cr^{+++}aq. is used in place of Cr^{++}aq., no CH_3OH is found in the distillate. Free CH_3OH added to a synthetic mixture containing the metal ions and acid is recovered almost quantitatively under the same conditions for distillation.

When pyrophosphate in excess is added to the mixture after reaction and the solution is subjected to continuous extraction with ether, in 6 hours 60–70% of the fumaric acid is recovered, this recovery being identical to that observed when RFH^{++} rather than $RFCH_3^{++}$ is the oxidant. The extract however contains very little alcohol (it should be noted that the half-ester would respond to the test for CH_3OH). If the reaction mixture then is refluxed to complete the complexing by pyrophosphate, the alcohol can be recovered essentially quantitatively on distillation.

From these and related observations, we conclude that ester hydrolysis accompanies electron transfer (to account for the appearance of acid and the extractability of fumaric acid) and that the CH_3OH is left coördinated to Cr(III) (to account for the holdback of alcohol by the solution). Blank experiments prove that CH_3OH in solution does not become associated with chromium when Cr^{++}-aq. reacts with RFH^{++}. Thus we conclude further that transfer of alcohol to chromium must be direct, and therefore that Cr^{++} attacks the ester end of the fumarato ligand.

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(2) D. K. Sebera and H. Taube, to be published (described in part in *Can. J. Chem.*, **37**, 129 (1959)).

DIFLUOROAMINE[1]

Sir:

During the reaction of nitrogen trifluoride with arsenic at elevated temperatures (250–300°) to produce tetrafluorohydrazine[2] small amounts of difluoroamine were produced.

The identity of difluoroamine has been established. Its molecular weight by vapor density measurements is 52 (calculated 53). The mass spectrum of difluoroamine given in Table I was obtained on a Consolidated Electrodynamics Model 620 Mass Spectrometer and is consistent with the formula HNF_2.

TABLE I

FRAGMENTATION PATTERN OF HNF_2

m/e	Ion	Pattern, %
53	HNF_2^+	100
52	NF_2^+	8.7
34	HNF^+	99.5
33	NF^+	47.4
20	HF^+	4.0
19	F^+	5.2
15	NH^+	8.7
14	N^+	23.0

The infrared absorption spectrum of difluoroamine consists of strong doublets at 7.0, 7.8, 10.2 and a triplet at 11.2μ. The n.m.r. proton spectrum consists of a triplet as would be expected from a proton spin–spin coupling with two equivalent fluorine nuclei. The center of the triplet is

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(1) Army Ordnance Contract DA-01-021-ORD-5135.

(2) C. B. Colburn and A. Kennedy, THIS JOURNAL, **80**, 5004 (1958).