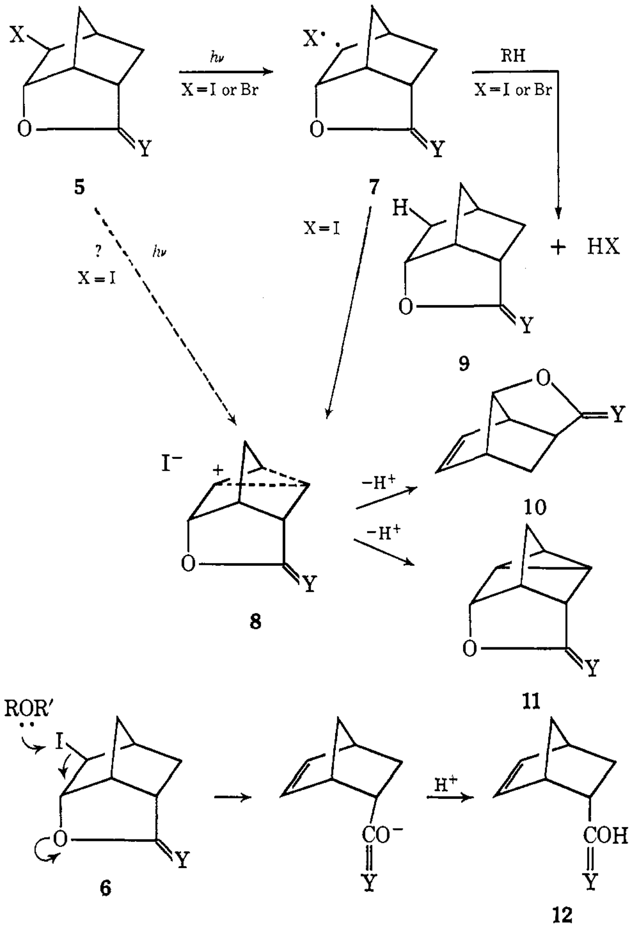
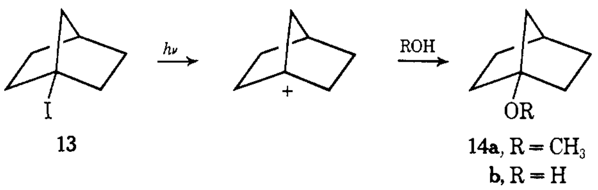
and nucleophilic substitution in the case of iodides strongly implies the involvement of cationic intermediates. It is not clear from the preliminary data whether these arise directly from excitation of the C–I chromophore or whether, as shown in Scheme I, excitation leads first to homolytic cleavage followed by an electron-transfer process. However, the concurrent formation of the reduction product **9** and the ionic products **10** and **11** makes the latter a tentatively attractive proposal. The difference in behavior between bromides and iodides is perhaps attributable to the difference in reactivity of Br· and I·. The former is a "hot" radical which probably undergoes rapid hydrogen abstraction from the solvent cage, leading to radical-type products, whereas the latter is incapable of abstracting hydrogen atoms from most solvents; in the absence of an efficient competing process in the latter case, the radical pair has sufficient lifetime for electron transfer to occur.

Scheme I



The powerfulness of the photochemistry of alkyl iodides for the facile generation of cations is seen by the rapid conversion of 1-iodonorborane (**13**)[12] to the ether **14a** (79%) and norbornane (8%) on irradation in methanol (2 hr). Under aqueous conditions the corresponding alcohol **14b**[13] is formed; presumably both products arise *via* generation and nucleophilic trapping of the 1-norbornyl cation.



The ring opening process leading to **12** ($Y = H_2$ or O) apparently proceeds *via* yet another mechanistic pathway, perhaps involving a nucleophilic attack by solvent on the excited state at iodine prior to homolytic dissociation, as indicated by **6**.[14] In view of the cleaness and rapidity of this photoreaction, it is a desirable alternative to the traditional zinc–acetic acid procedure for the opening of iodo lactones and ethers.[15]

It is clear that alkyl iodides display a rich array of photochemical behavior, much of it having synthetic as well as mechanistic interest. Continued studies are in progress to delineate further both aspects of the photobehavior of a wide variety of organic iodides.

Acknowledgment. Partial support of this work by the Research Corporation is gratefully acknowledged, as is the assistance of T. Randall Fields with some of the initial experiments.

[12] P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Amer. Chem. Soc.*, **88**, 78 (1966).

[13] D. B. Denney and R. R. DiLeone, *ibid.*, **84**, 4737 (1962).

[14] A free-radical fragmentation process does not seem likely, at least for the lactone **5** ($X = I$; $Y = O$), in view of the well-known propensity of the carboxyl radical for undergoing decarboxylation.

[15] C. S. Rondestvedt, Jr., and C. D. Ver Nooy, *J. Amer. Chem. Soc.*, 77. 4878 (1955).

[16] Alfred P. Sloan Research Fellow.

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Three-Electron Oxidations. IV. Chromic Acid Cooxidation of Tertiary Hydroxy Acids and Alcohols[1,2]

Sir:

We have recently reported[3] a dramatic rate acceleration of two to three orders of magnitude observed in the chromic acid oxidation of a two-substrate system of isopropyl alcohol and oxalic acid. The results lead us to propose a mechanism consisting of the formation of a termolecular complex and its decomposition in a single-step three-electron oxidation reaction.

We have now obtained evidence showing that the ability to undergo rapid cooxidation in the presence of alcohols is not restricted to oxalic acid, but is shared by numerous other compounds, most notably by hydroxy acids.[4]

The pseudo-first-order rate constant for the chromic acid oxidation in aqueous perchloric acid (0.628 *M*) at 60° is 1.16×10^{-4} sec^{-1} for α-hydroxyisobutyric acid (0.156 *M*) and 1.65×10^{-4} sec^{-1} for 2-hydroxy-2-methylbutyric acid (0.170 *M*). Under the same conditions, the pseudo-first-order rate constant for a 0.039 *M* solution of isopropyl alcohol is 1.16×10^{-3} sec^{-1}. However, a mixture containing isopropyl alcohol and either of the hydroxy acids, all in the concentrations given above, reacts considerably faster: $k = 5.78 \times$

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[1] Part III: F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **94**, 8946 (1972).

[2] This investigation was supported by the National Science Foundation.

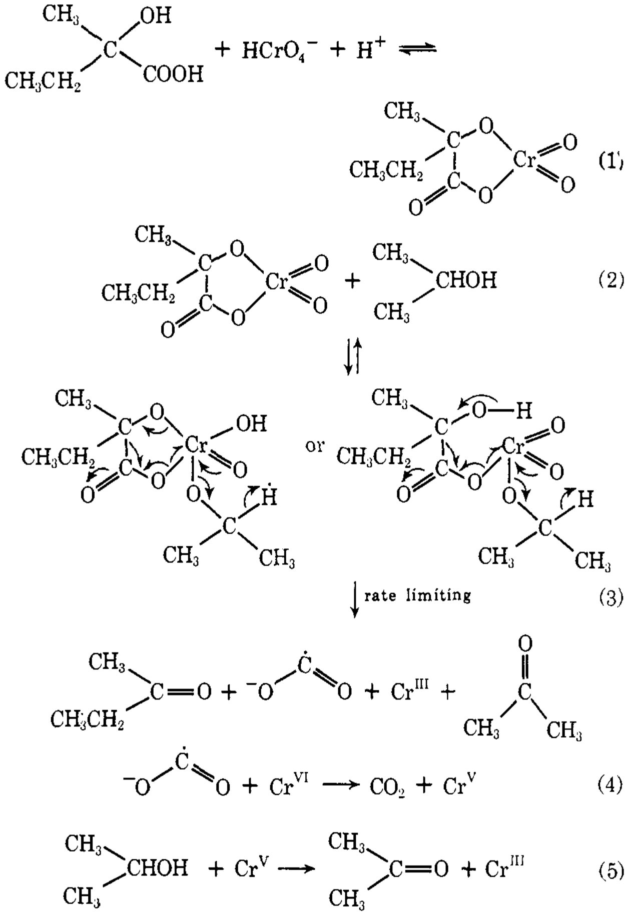
[3] F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **94**, 3181 (1972).

[4] F. Hasan and J. Roček, unpublished results.

Table I. Products of Cooxidation of Isopropyl Alcohol and 2-Hydroxy-2-methylbutyric Acid

[Isopropyl alcohol], *M*	[Hydroxy acid], *M*	[Acrylonitrile], *M*	[HClO$_4$], *M*	Cr(VI), mmol	Acetone, mmol	Methyl ethyl ketone, mmol	CO$_2$, mmol
0.780	0.617	0.0	0.628	1.57	1.61	0.72	0.69
0.780	0.617	0.396	0.628	1.57	1.60	1.54	0.0

Scheme I



10^{-3} sec^{-1} for α-hydroxyisobutyric acid and $k = 8.25 \times 10^{-3}$ sec^{-1} for 2-hydroxy-2-methylbutyric acid. These rate constants are 4.5 and 6.2 times greater than the sums of the rate constants for the two substrates (1.28×10^{-3} and 1.33×10^{-3} sec^{-1}), respectively. Similar rate accelerations have been obtained for citric acid and also for secondary hydroxy acids like malic, *meso*-, and *d*-tartaric acids and to a somewhat lesser extent for glycolic and lactic acids.[4]

The products obtained in the chromic acid oxidation of a mixture of isopropyl alcohol and 2-hydroxy-2-methylbutyric acid in the absence and in the presence of acrylonitrile used as a free-radical scavenger[5] are given in Table I.

In both cases both substrates undergo oxidation and the isolated products account for all chromium(VI) used. However, in the presence of acrylonitrile no carbon dioxide was produced, and acetone and methyl ethyl ketone were formed in a 1 : 1 ratio. The suppression of the carbon dioxide formation in the presence of the free-radical scavenger indicates that all CO$_2$ is formed *via* a free-radical intermediate.

The mechanism of the chromic acid oxidation of a mixture of isopropyl alcohol and 2-hydroxy-2-methylbutyric acid can best be represented by Scheme I. The rate-limiting step (reaction 3) consists of a decomposition of the termolecular complex into a chromium(III) species, one molecule of acetone, one molecule of methyl ethyl ketone, and a free-radical $\cdot CO_2^-$. In the presence of acrylonitrile this free radical is trapped and removed from the reaction chain. In the absence of the free-radical scavenger the radical is oxidized by chromium(VI) to carbon dioxide (reaction 4). The chromium(V) species formed in this reaction then reacts with isopropyl alcohol to give another molecule of acetone (reaction 5),[7] leading thus to an overall product ratio of acetone:methyl ethyl ketone:carbon dioxide of 2:1:1.

The large number of compounds capable of accelerating the reduction of chromic acid by isopropyl alcohol[4] and the composition of the reaction products reported in this communication strongly indicate that three-electron cooxidations may represent a rather general and important new class of oxidation reactions.

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(5) Acetone and methyl ethyl ketone were separated as the 2,4-dinitrophenylhydrazones by column chromatography,[6] on a 1 : 1 mixture of Bentonite (Fisher) and infusorial earth (Fisher) with chloroform and chloroform–ethanol (1 : 1) as eluents. The compounds were identified by comparison with authentic samples. Carbon dioxide was determined manometrically in a Warburg apparatus.[3]

(6) J. A. Elvidge and M. Whalley, *Chem. Ind.* (*London*), 589 (1955).

(7) In principle, chromium(V) could also react with 2-hydroxy-2-methylbutyric acid to give another molecule of methyl ethyl ketone and of carbon dioxide. However, since the rate of the chromium(VI) oxidation of 2-hydroxy-2-methylbutyric acid is much lower than that of isopropyl alcohol and since relative reactivities of chromium(VI) and chromium(V) have been found to be quite similar,[8] chromium(V) is likely to react almost exclusively with isopropyl alcohol.

(8) K. B. Wiberg and H. Schäfer, *J. Amer. Chem. Soc.*, 91, 933 (1969).

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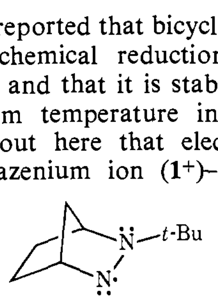
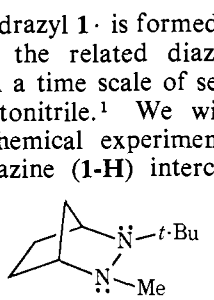
Electrochemical Estimation of the Acidity of a Trialkylhydrazine

Sir:

We reported that bicyclic hydrazyl **1**· is formed upon electrochemical reduction of the related diazenium salt **1**$^+$ and that it is stable on a time scale of seconds at room temperature in acetonitrile.[1] We wish to point out here that electrochemical experiments on the diazenium ion (**1**$^+$)–hydrazine (**1-H**) interconversion require that the trialkylhydrazine **1-H** is a remarkably weak acid. The cycle shown in Scheme I con-



1·



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(1) S. F. Nelsen and R. T. Landis, II, *J. Amer. Chem. Soc.*, submitted for publication.