further experimental details, will be presented in a full paper.

[15] National Science Foundation Undergraduate Research Participant, 1964–1965.

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Free-Radical Intermediates in Chromic Acid Oxidation

Sir:

A previous report from this laboratory[1] noted a small amount of polymerization of acrylonitrile added to a chromic acid oxidation of phenyl-*t*-butylcarbinol (2,2-dimethyl-1-phenyl-1-propanol). The polymerization occurred under conditions which lead to the formation of relatively large (~50%) amounts of the "cleavage" products, benzaldehyde and *t*-butyl alcohol. It was noted that the conversion to polymer was low (approximately 0.020 g for 20 ml of 0.025 *M* CrO_3 solution) and the product ratios were unchanged from oxidations under the same conditions but without acrylonitrile. The source and nature of the radicals initiating the polymerization could not be identified. We have now found that these radicals result from the oxidation of benzaldehyde by an intermediate Cr(IV) [most probable] or Cr(V) species.

No polymer could be detected in the oxidation of 2-propanol under the same conditions. However, the dropwise addition of 10 ml of a solution of CrO_3 (0.05 *M* in 85% aqueous acetic acid) to a solution containing 1 ml of 2-propanol, 1 ml of benzaldehyde, 5 ml of acrylonitrile, and 15 ml of the 85% aqueous acetic acid led to precipitation of the polymer within 15 min. The precipitation continued as long as the addition was continued (about 6 hr). Two grams of film-forming polymer was isolated. In the absence of the 2-propanol, polymer precipitation was delayed for several hours and only poor conversions were obtained over 48 hr (0.050 g). Omission of the benzaldehyde under the above conditions led to no polymer formation. These data suggest that the intermediate Cr(IV) or Cr(V) species formed in the oxidation of the alcohol[2] was responsible for the radical products and that the oxidation of benzaldehyde was involved in the initiation. These Cr(IV) and Cr(V) species are formed much more slowly in the oxidation of benzaldehyde than in the oxidation of a secondary alcohol.

When extra benzaldehyde was added to the oxidation of phenyl-*t*-butylcarbinol, the benzaldehyde was oxidized at a much greater rate than was observed for Cr(VI) alone. The extent of this secondary oxidation was dependent on the amount of benzaldehyde added. This is characteristic of previously observed "induced oxidations" by Cr(IV) and Cr(V).[2–4] As would be expected for this interpretation, the polymerization reaction was completely eliminated by the addition of Ce(III) to the oxidation. The Ce(III) removes the lower oxidation states of chromium from the reaction.[2,5]

In view of the above, it should be noted that Wiberg and Richardson[3] reported that ~30% yields of carbon monoxide could be obtained by the Cr(VI) oxidation of triphenylacetaldehyde, probably by decarbonylation of the radical formed by attack of Cr(IV) on the triphenylacetaldehyde.

In a full publication which is in preparation, we will relate these observations to the mechanisms of chromic acid oxidations of alcohols and aldehydes. The one-electron reagent is identified as Cr(IV) in the above cases. If Cr(V) acted as a one-electron reagent (reaction 1), the reaction would be an autocatalytic chain reaction due to reaction 2. Since these aldehyde oxidations are not autocatalytic,[3,6,7] this process cannot occur to any appreciable extent.

$$\mathrm{Cr(V)} + \text{substrate} \longrightarrow \mathrm{Cr(IV)} + \text{radical} \tag{1}$$

$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \longrightarrow 2\mathrm{Cr(V)} \tag{2}$$

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[1] W. A. Mosher, W. H. Clement, and R. L. Hilliard, "Selective Oxidation Processes," Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965, pp 81–88.

[2] J. Hampton, A. Leo, and F. H. Westheimer, *J. Am. Chem. Soc.*, 78, 306 (1956).

[3] K. B. Wiberg and W. H. Richardson, *ibid.*, 84, 2800 (1962).

[4] J. Rocek and A. Riehl, *Tetrahedron Letters*, 1437 (1966).

[5] The quenching of Cr(IV) and Cr(V) reactions by Ce(III) is more complicated than previously indicated. This subject will be included in a future publication.

[6] K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 3022 (1958).

[7] G. T. E. Graham and F. H. Westheimer, *ibid.*, **80**, 3030 (1958).

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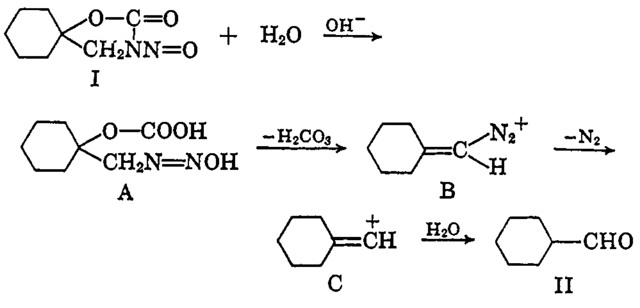
Unsaturated Carbenes Formed by Reaction of Nitrosooxazolidones with Bases

Sir:

Some time ago a mechanism was proposed to account for the products produced in the alkaline decomposition of nitrosooxazolidones in which an unsaturated carbonium ion was the key intermediate.[1] This mechanism is illustrated below in the reaction of 3-nitroso-1-oxa-3-azaspiro[4.5]decan-2-one (I) with hydroxide ion to yield formylcyclohexane (II). The hypothetical species involved were A, B, and C.



All of the products isolated in this and other cases[2,3] could be satisfactorily accounted for by assuming that unsaturated carbonium ions similar to C were involved. In his book,[4] Hine suggested that by a different mechanism A could decompose *via* an unsaturated diazo compound (E) to yield an unsaturated carbene (F) which could then give rise to products.

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[1] M. S. Newman and A. Kutner, *J. Am. Chem. Soc.*, 73, 4199 (1951). As in the present paper, the timing of proton movements was ignored.

[2] M. S. Newman and W. M. Edwards, *ibid.*, 76, 1840 (1954).

[3] M. S. Newman and A. E. Weinberg, *ibid.*, 78, 4654 (1956).

[4] J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964, pp 89–90.