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THE MECHANISM OF THE CHROMIC ACID OXIDATION OF HYDROCARBONS

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IN the acid catalyzed oxidation of a hydrocarbon by chromic acid in aqueous acetic acid a tertiary alcohol is formed if the starting material contained a tertiary C-H group;[1] if only methylene groups were initially present, then a ketone is formed.[2] If the formation of the new C-O bond and the cleavage of the C-H bond occurred simultaneously (by hydrogen displacement or oxygen insertion), the transition state would be crowded. Since the reaction is rather insensitive to steric hindrance,[3] a concerted mechanism appears improbable. Moreover, the rates of chromic acid oxidation of hydrocarbons parallel those for the solvolysis of the corresponding tosylates,[2] which suggests that a tricovalent intermediate is formed. However, attempts to prove the existence of an intermediate carbonium ion or free radical have usually been unsuccessful.

For example, no tetraphenylethane (which could be formed from radicals) can be isolated in the oxidation of diphenylmethane.[4] The oxidation of cycloalkanes in acetic acid yields ketones, and not cycloalkyl acetates[2] which would be formed from carbonium ions under the conditions employed;

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[1] W.F. Sager and A. Bradley, J. Amer. Chem. Soc. 78, 1187 (1956; J. Roček, Coll. Czech. Chem. Comm. 23, 833 (1958).

[2] F. Mares, J. Roček and J. Sicher, Coll. Czech. Chem. Comm. 26, 2355 (1961).

[3] F. Mareš and J. Roček, Coll. Czech. Chem. Comm. 26, 2370 (1961).

[4] K.B. Wiberg and R.J. Evans, Tetrahedron 8, 313 (1960).

methyl cyclohexane yields mainly methyl cyclohexanol,[5] even when the reaction is carried out in anhydrous acetic acid. Furthermore, tertiary hydrocarbons are oxidized to the corresponding alcohols with retention of configuration,[6] demonstrating that neither a carbonium ion nor a radical is free during the oxidation process.

In order to rationalize these facts, the oxidation has been depicted as proceeding by way of a complex consisting either of a carbonium ion[3] and chromium (IV), or alternatively of a radical[6] and chromium (V). In either case, an intermediate must exist which retains configuration, and then collapses presumably to an ester of tetravalent chromium. However, neither of these structures is altogether satisfactory. The first alternative predicts anchimeric assistance in the oxidation of camphane, isocamphane, cyclobutane and 2,2,3,4,4-pentamethylpentane; none is observed.[2,3] The second alternative does not explain what forces can hold together an electrically neutral radical and the (probably cationic) chromium (V), in a rather polar medium. Moreover, it is questionable whether the transfer of an electron from the easily oxidized free radical to the strong oxidizing agent, chromium (V), within the complex would require any activation energy at all. Unless specific reasons for the stability of a structure of this type could be found, one might be more inclined to regard it as a representation of a transition state rather than of an intermediate. The description of the reaction intermediate as being formed by a free radical and a chromium (V) species, also does not help to understand why carbonium ions do become free in some special cases as in the oxidation of 2,2-dimethylbutane where roughly equal amounts of pinacolone and acetone are

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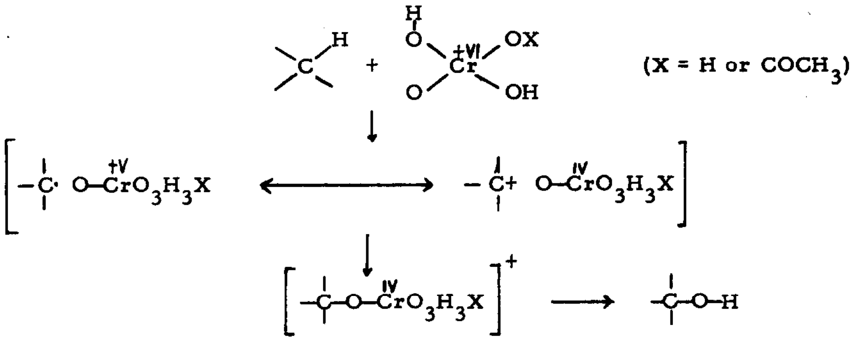
[5] P. Kouřím and R. Tykva, Coll. Czech. Chem. Comm. 26, 2511 (1961).

[6] K.B. Wiberg and G. Foster, J. Amer. Chem. Soc. 83, 423 (1961); P.v.R. Schleyer and R.D. Nicholas, Abstracts of the 140th Meeting of the American Chemical Society, Chicago, 1961, p. 75Q

formed.[3] The latter evidently results from the further oxidation of a rearrangement product of the pinacolyl cation. Carbonium ions have also been "trapped" as azides, if the oxidation was carried out in the presence of azide ions.[7] All these features can be more easily understood on the basis of a carbonium ion - chromium (IV) complex, assuming that it is held together by ion-dipole forces and can dissociate to an extent determined primarily by the properties of the carbonium ion.[8]

We believe that the difficulties of each of these descriptions can be over come by regarding the intermediate as a mesomeric hybrid of the two pairs just discussed. Since the hybrid would have a lower energy than either extreme structure, the stability of such an intermediate is reasonable. With this assumption, the mechanism of the chromic acid oxidation of hydrocarbons may be represented by the following scheme:



Chromic acid has been written in the protonated form and in equilibrium with its mixed anhydride with acetic acid in order to account for acid catalysis and for the strong increase in rate with increase in the concen-

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[7] I. Nescoiu and C.D. Nenitzescu, Chem. & Ind. 377 (1960).

[8] As pointed out by the referee, an anomalous[9] carbon-oxygen fission of the chromium (IV) ester could provide an alternative source for carbonium ions.

[9] K.B. Wiberg and G. Foster, Chem. & Ind. 108 (1961).

tration of acetic acid in the solvent.[10] The resonance between the two structures shown above is allowed, since they contain the same number of unpaired electrons. The chromium (IV) compound, in analogy with $Cr(O\text{-}t\text{-}C_4H_9)_4$, presumably has two unpaired electrons;[11] in the radical-chromium (V) structure, the metal ion and the organic moiety each have one unpaired electron.

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[10] J. Roček, *Coll. Czech. Chem. Comm.* **22**, 1509, 1519 (1957).

[11] N. Hagihara and H. Yamazaki, *J. Amer. Chem. Soc.* **81**, 3160 (1959).