Mechanism of Oxidation of Saturated Hydrocarbons by Lead(IV), Cobalt(III), and Manganese(III) Trifluoroacetates

By STEPHEN R. JONES and JOHN M. MELLOR*
(*Department of Chemistry, The University, Southampton* SO9 5NH)

Summary Comparison of the oxidation of a series of substituted adamantanes by lead(IV), cobalt(III), and manganese(III) trifluoroacetates with studies of anodic oxidation shows that electrochemical oxidation, but not oxidation with the metal salts, proceeds *via* cation radical intermediates.

OXIDATION of saturated hydrocarbons by salts of transition metals is a subject of considerable industrial importance, and recently of mechanistic studies.[1] Cation radical intermediates have been proposed in both the oxidation of aromatic[2] and saturated[1] hydrocarbons. With aromatic hydrocarbons the proposition is based on spectroscopic and kinetic evidence and product studies, but with saturated hydrocarbons the proposition is based solely on kinetic evidence. In view of the difficulty in interpreting these kinetic studies we have now made a product analysis of the oxidation of a series of substituted adamantanes and conclude that with these hydrocarbons, having low ionisation potentials and therefore particularly susceptible to oxidation, there is no evidence that cation radicals are formed as intermediates in the oxidations with transition-metal salts.

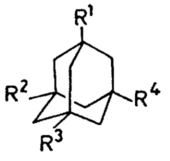
TABLE. Products of oxidation of substituted adamantanes

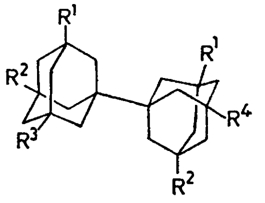
Compound[a]	Ionisation[b] potential (eV)	Oxidant	Product[c] and yields (%) Substitution	Fragmentation
(**1**)	9·06	Anode MeCN[d]	(**4**) 77	—
(**2**)	8·96	Anode MeCN[d]	(**5**) 7	(**6**) 62
(**2**)	8·96	Anode CF_3CO_2H[e]	(**7**) 36	(**8**) 26, (**9**) 21
(**2**)	8·96	Pb^{4+} [f]	(**7**) 86	(**8**) $< 0{\cdot}1$
(**3**)	8·90	Anode MeCN[d]	—	(**10**) 91
(**3**)	8·90	Anode CF_3CO_2H[e]	—	(**11**) 90
(**3**)	8·90	Pb^{4+},[f]Mn^{3+} or CO^{3+}	Slow reaction complex products[g]	
(**12**)	8·50	Anode MeCN[d]	(**14**) $< 0{\cdot}1$, (**16**) $< 0{\cdot}1$	(**18**) 80
(**12**)	8·50	Pb^{4+} [f]	(**15**) 68, (**17**) 11	(**19**) $< 0{\cdot}1$
(**12**)	8·50	$Mn_3{}^+$ [h]	(**15**) 77, (**17**) 8	(**19**) 1
(**12**)	8·50	Co^{3+} [h]	(**15**) 76, (**17**) 8	(**19**) $< 0{\cdot}1$
(**13**)		Mn^{3+} or Co^{3} +	Slow reaction, complex products[g]	
(**12**)	8·50	Anode CF_3 CO_2H[e]	(**15**) 12, (**17**) 3	(**19**) 32, (**20**) 10, (**21**) 12

[a] Syntheses will be described in subsequent publications. [b] Measured by photoelectron spectroscopy using a Perkin–Elmer PS18 instrument. [c] Products characterised by g.l.c. comparison with authentic samples;[a] yields based on hydrocarbon consumed. [d] Conditions described in ref. 4. [e] Controlled potential electrolysis at *ca.* 1·7 V at a platinum anode with respect to a silver wire electrode. [f] Reaction at 20 °C in CF_3CO_2H–CH_2Cl_2 (1 : 1) for 1·5 h; reaction greatly accelerated by traces of Cl^-. CH_2Cl_2 is added to permit better solution of hydrocarbons; it has little effect on products. [g] Typically after prolonged reaction times $< 10\%$ hydrocarbon is consumed and g.l.c. analysis shows that there are more than ten products in the reaction mixture. [h] Reaction at 75 °C in CF_3CO_2H–CH_2Cl_2 (1 : 1) for 6 h in sealed tube.

The results of electrochemical oxidation and oxidation with transition metal salts are compared in the Table.

The delocalized[3] cation radicals of certain adamantanes undergo characteristic fragmentation.[4] Thus generation of the cation radical of t-butyladamantane anodically leads preferentially to products of fragmentation [N-(1-adamantyl)acetamide in acetonitrile and adamantyl trifluoroacetate in trifluoroacetic acid] and, only by a minor pathway, to disubstituted adamantanes by proton loss. In CF_3CO_2H, the solvent for oxidations with the metal salts, the electrochemical oxidation is complicated by the secondary process of intermolecular hydride transfer evidenced by formation of (**9**) and (**20**). However, when the leaving group is tertiary, fragmentation is the dominant primary oxidation process both in CF_3CO_2H and in MeCN where hydride shifts are unimportant. Oxidation of the same adamantanes by lead(IV), cobalt(III), or manganese(III) trifluoroacetates gives only products formed by attack at a carbon–hydrogen bond. We conclude from the absence of products of fragmentation that attack by the metal salts takes place at a carbon–hydrogen bond and does not proceed *via* the delocalized cation radical. The possibility that a cation radical is formed in the oxidations by the metal salts, but that the behaviour of the resultant cation radical is different at the electrode and in solution, is considered to be an inadequate explanation of our results. In contrast to mono-, di-, and tri-substituted adamantanes which are oxidised smoothly with, *e.g.* Pb^{4+}, tetrasubstituted adamantanes, where a cation radical might undergo fragmentation, are found to be quite unreactive. We conclude that with metal salts oxidation proceeds by direct attack at a carbon–hydrogen bond. In our work both the nature of the hydrocarbon (low ionisation potential) and the choice of solvent (giving metal salts of high electron affinity) might be expected to favour formation of cation radicals. Their absence in this work suggests that in other studies[1] either using hydrocarbons less susceptible to formation of cation radicals (*e.g.* cyclohexane) or using acetic acid as solvent, the observed oxidation of saturated hydrocarbons also proceeds *via* attack at a carbon–hydrogen bond and not *via* cation radical intermediates.





(**1**) $R^1=R^2=R^3=H$; $R^4=Et$
(**2**) $R^1=R^2=R^3=H$; $R^4=Bu^t$
(**3**) $R^1=R^2=R^3=Me$; $R^4=Bu^t$
(**4**) $R^1=R^2=H$; $R^3=NHCOMe$; $R^4=Et$
(**5**) $R^1=R^2=H$; $R^3=NHCOMe$; $R^4=Bu^t$
(**6**) $R^1=R^2=R^3=H$; $R^4=NHCOMe$
(**7**) $R^1=R^2=H$; $R^3=OCOCF_3$; $R^4=Bu^t$
(**8**) $R^1=R^2=R^3=H$; $R^4=OCOCF_3$
(**9**) $R^1=R^2=R^3=R^4=H$
(**10**) $R^1=R^2=R^3=Me$; $R^4=NHCOMe$
(**11**) $R^1=R^2=R^3=Me$; $R^4=OCOCF_3$
(**18**) $R^1=R^2=Me$; $R^3=H$; $R^4=NHCOMe$
(**19**) $R^1=R^2=Me$; $R^3=H$; $R^4=OCOCF_3$
(**20**) $R^1=R^2=Me$; $R^3=R^4=H$
(**21**) $R^1=R^2=Me$; $R^3=R^4=OCOCF_3$

(**12**) $R^1=R^2=Me$; $R^3=R^4=H$
(**13**) $R^1=R^2=R^3=R^4=Me$
(**14**) $R^1=R^2=Me$; $R^3=H$; $R^4=NHCOMe$
(**15**) $R^1=R^2=Me$; $R^3=H$; $R^4=OCOCF_3$
(**16**) $R^1=R^2=Me$; $R^3=R^4=NHCOMe$
(**17**) $R^1=R^2=Me$; $R^3=R^4=OCOCF_3$

We thank the S.R.C. for financial support.

(*Received*, 19*th February* 1976; *Com.* 177.)

---

[1] R. Tang and J. K. Kochi, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3845; J. Hanotier, P. Camerman, M. Hanotier-Bridoux, and P. de Radzitzky, *J.C.S. Perkin II*, 1972, 2247; J. Hanotier and M. Hanotier-Bridoux, *ibid.*, 1973, 1035; J. Hanotier, M. Hanotier-Bridoux, and P. de Radzitzky, *ibid.*, 1973, 381; A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.*, 1973, **38**, 909 and 3729.

[2] E. I. Heiba, R. M. Dessau, and W. J. Koehl, *J. Amer. Chem. Soc.*, 1969, **91**, 6830; J. K. Kochi, R. Tang, and T. Bernath, *ibid.*, 1973, **95**, 7114.

[3] W. Schmidt, *Tetrahedron*, 1973, **29**, 2129.

[4] G. J. Edwards, S. R. Jones, and J. M. Mellor, *J.C.S. Chem. Comm.*, 1975, 816.