Reactions of Alcohols Adsorbed on Montmorillonite and the Role of Minerals in Petroleum Genesis

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IT has been suggested[1,2] that catalytic reactions of organic substrates on mineral surfaces are contributory processes in petroleum genesis. This thesis is supported by observations[3,4] on the behaviour of alkanes and alkenes on silica–alumina catalysts, which undergo complex reactions including polymerization, cracking, isomerization, and hydrogen-transfer processes, to give a complex mixture of hydrocarbon products. The systems studied in the laboratory have often involved synthetic catalysts and the products include appreciable yields of olefins which, however, constitute[2] a negligible proportion of natural petroleum, The present work was undertaken to extend the understanding of catalytic properties of natural minerals, through investigation of the thermal desorption reactions of alcohols and of alkenes adsorbed at 20° on a sample of natural montmorillonite. The experimental techniques have been described;[5] mild experimental conditions ($<250°$) were used. No detectable hydrocarbon was given by this sample of montmorillonite under reaction conditions in the absence of added organic compounds.

Thermal desorption measurements, with continuous product condensation at $-195°$ during reaction, gave the following results. Chemisorbed n-hexanol yielded $4{\cdot}0 \times 10^{16}$ mol.g.$^{-1}$ of an equilibrium mixture of n-hexene isomers by a reaction with activation energy 24·0 kcal. mole^{-1} (90—195°); there was no appreciable cracking $<200°$. The behaviour of n-dodecanol and n-octadecanol were both almost identical; significant cracking to form n-C_5—n-C_8 alkenes occurred $<200°$. Both reactants yielded (*inter alia*) $4{\cdot}0 \times 10^{17}$ mol.g.$^{-1}$ of an equilibrium mixture of n-hexene isomers by a rate process having similar kinetic characteristics (120—210°) to that found for production of hexene isomers from hexanol. The products from the reactions of adsorbed heptadec-1-ene and of octacosane were closely similar to those found for the long-chain alcohols. All the reactants studied yielded mixtures of n-alkenes as the only significant products.

Studies were also made of the thermal desorption reactions of adsorbed n-hexanol and n-dodecanol where products were not continually condensed at $-195°$. Here readsorption of primary products of reaction and water vapour (contained in the montmorillonite sample) was possible. Results showed that complex surface processes, including polymerization, cracking and isomerization, occurred to give a product mixture consisting predominantly of isoalkanes (C_4 to at least C_8) from reaction $<200°$. Only a small proportion of n-alkanes were formed and yields of n-alkenes were negligible. The rate of this reaction at $\sim180°$ was comparable to that of alcohol dehydration, a detailed kinetic investigation has not yet been completed.

The olefin production reaction can be explained by a mechanism in which the organic reactant was initially adsorbed at a Lewis-acid site on the largely dehydrated montmorillonite (aluminosilicate) surface. Subsequent reactions were limited to cracking and double-bond migration. The reaction products were, however, different where water and product olefin removal was not rapid and the formation of isoalkanes may be ascribed[4] to the activity of Brønsted-acid sites on the surfaces of the clay particles. We thus conclude that the reaction of water vapour with superficial acid sites on this mineral was more rapid than such processes on activated (heat-treated) synthetic silica–alumina.

Extrapolation of kinetic data for olefin production showed that, assuming a zero-order catalytic reaction, the theoretical yield from this natural montmorillonite at 20° was 0·01 g. hexenes from 1·00 g. reactant in 6800 (270,000; 325,000) years from n-hexanol (n-dodecanol; n-octadecanol). There was evidence that the rate of isoalkane production was comparable. The closely similar kinetic characteristics of hexene desorption indicate that product removal from the surface was the rate-limiting process. Under natural conditions, organic substances may be chemisorbed on the active surfaces of finely divided clay particles while these aluminosilicates are in contact with the biosphere, in the soil or during weathering. Furthermore, the organic complexes retained by the clays, during their residence in the soil, may become progressively enriched in those compounds which are most strongly bonded to the aluminosilicate surface. The present observations showed that montmorillonite retained alcohols while appreciable amounts of water were desorbed during evacuation at 20°. Strongly bonded surface complexes may remain in the clay after burial in sediments and these are subsequently desorbed through rate processes of the type described above, which were studied at 100—200°. Thus, we may conclude that this widely distributed clay mineral possessed sufficient catalytic activity for hydroxy-group removal, with subsequent production of mixtures of isoalkanes, to explain the transformation of appropriate organic material, deposited in sediments, into petroleum constituents.

Studies were also made of the thermal desorption reaction of a sample of iron-rich peat (14·6% Fe, from a remote site in North-West Scotland). Products identified included benzene, toluene, n-hexane, and n-heptane. The activation energy for benzene production was 23·4 kcal. mole^{-1} (170—270°) and the total yield was $4{\cdot}0 \times 10^{17}$ mol. g.$^{-1}$. Extrapolation of these data showed that this reaction could also give an appreciable benzene yield in geological periods of time (1% in 2×10^{7} years at 20°). The kinetic characteristics of benzene production were identical (within experimental error) with those found for benzene production from alcohols on ferric oxide[6] and it is concluded that the rate-limiting steps in both processes were identical. The more stable constituents of the peat are expected to be incorporated in deposited material which may contribute to buried sediments.

The present results show that desorption of adsorbed material from clay minerals and from ferric oxide yield alkanes and aromatic hydrocarbons, respectively. We suggest that organic compounds, chemisorbed on mineral particles while in contact with the biosphere, represents a significant fraction of the carbonaceous material which is ultimately incorporated in buried sediments. The rate of decomposition of these adsorbed species is sufficiently great to account for the production of petroleum deposits in geological periods of time, without the necessity of an external heat source. We conclude, therefore, that reactions at mineral surfaces provide a significant, if not the dominant, route for petroleum production from organic matter contained in sediments.

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[1] A. I. Levorsen, "Geology of Petroleum", Freeman, San Francisco, 1965, ch. 11; P. F. Andreev, A. I. Bogomolov, A. F. Dobryanskii, and A. A. Kartsev, "Transformation of Petroleum in Nature", Translation, Pergamon, Oxford, 1968; W. Henderson, G. Eglinton, P. Simmonds, and J. E. Lovelock, *Nature*, 1968, **219**, 1012.

[2] K. B. Krauskopf, "Introduction to Geochemistry", McGraw-Hill, New York, 1967, ch. 11.

[3] C. Kemball and J. J. Rooney, *Proc. Roy. Soc.*, 1960, *A*, **257**, 132; 1961, **263**, 567; Y. Kubokawa, *J. Phys. Chem.*, 1965, **69**, 2676.

[4] F. E. Shephard, J. J. Rooney, and C. Kemball, *J. Catalysis*, 1962, **1**, 379.

[5] A. K. Galwey, "Proceedings, Third International Congress on Catalysis, Amsterdam, 1964", North-Holland Publishing Co., Amsterdam, 1965, p. 791; *J. Catalysis*, 1965, **4**, 34.

[6] A. K. Galwey, *J. Catalysis*, 1968, **21**, 352.