436. *Liquid-phase Oxidation of Hex-*1*-ene*

By S. J. Moss and H. Steiner

Hex-1-ene was oxidised to an extent of about ten per cent by molecular oxygen in propionic acid with cobalt salts as catalysts. The major products, are hexene-epoxide, -glycol, glycol- and hexenyl-esters, hexenal, hexenoic acid, and carbon dioxide. By co-oxidation of hex-1-ene and cyclohexene evidence was obtained supporting the mechanism of epoxidation suggested by Twigg. Within the limitations of the analytical methods used, all unsaturated oxidation products were found to be derivatives of hex-2-ene, hex-1-ene derivatives being absent. An explanation of this result is suggested.

Although the liquid-phase oxidation of olefins by oxygen has been investigated considerably,[1,2] certain areas in this field require further exploration. A point of uncertainty is, for instance, the mechanism of the formation of epoxides. which in many cases appear simultaneously with alkenyl hydroperoxides and their decomposition products.[3-6] It is also known that, with olefins of from three to ten carbon atoms, the commonly accepted Bolland mechanism [1,2] of olefin oxidation fails to explain all the experimental facts and must be modified or extended.[6b,7]

These reasons prompted us to study the oxidation of hex-1-ene. Most experiments were carried out in propionic acid with cobalt propionate as catalyst; at between 80 and 85°. We found as main products amounting to nearly 70% of the converted hexene, 1,2-epoxyhexane and its derivatives, and also unsaturated compounds, such as hex-2-en-1-al, hex-2-en-1-yl propionate and hex-2-enoic acid. The latter group of compounds must be considered as the products of decomposition or of further oxidation, of hex-2-en-1-yl hydroperoxide or of the corresponding hydroperoxy- or alkenoxy-radical. Both groups of compounds appear to be formed simultaneously in a ratio of 0·7 : 1 (Table 1).

Thus, in this case peroxidation and epoxidation run roughly parallel to each other. In previous investigations the epoxides and their derivatives were obtained in good yield, but the hydroperoxy-derivatives were often degraded to compounds of lower molecular weight.[3-6]

The simultaneous occurrence of peroxidation and epoxidation is explained by the

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[1] (*a*) J. L. Bolland, *Quart. Rev.*, 1949, **3**, 1; (*b*) L. Bateman, *ibid.*, 1954, **8**, 147.

[2] (*a*) C. Walling, " Free Radicals in Solution," Wiley, New York, 1957, ch. 9; (*b*) E. G. E. Hawkins, " Organic Peroxides," Spon, London, 1961, ch. 12.

[3] G. H. Twigg, *Chem. Eng. Sci.*, 1954, **3**. Special Suppl., p. 5; *Chem. and Ind.*, 1962, 4.

[4] E. J. Gasson, A. F. Millidge, G. R. Primavesi, W. Webster, and D. P. Young, *J.*, 1954, 2161; E. J. Gasson, A. F. Millidge, and W. Webster, B.P. 682,067/1952.

[5] E. G. E. Hawkins and D. C. Quinn, *J. Appl. Chem.*, 1956, **6**, 1.

[6] (*a*) W. F. Brill, *J. Amer. Chem. Soc.*, 1963, **85**, 141; (*b*) W. F. Brill and B. J. Barone, *J. Org. Chem.*, 1964, **29**, 140.

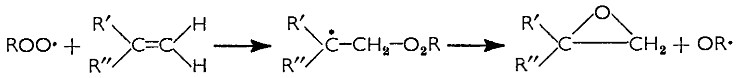
[7] K. R. Hargrave and A. L. Morris, *Trans. Faraday Soc.*, 1956, **52**, 89.

TABLE 1

Products	Yield relative to hexene charged [a] (mmoles/mole)	Yield relative to hexene consumed [a] (mole-%)
1,2-Epoxyhexane	6·7	8·0
Hexane-1,2-diol	9·9	11·8
Hex-2-en-1-al	8·3	9·9
Hex-2-enoic acid	15·5	18·3
Hexane-1,2-diol dipropionate	4·0	4·8
Hex-2-en-1-yl propionate	7·0	8·3
Polymer	3·1	15·1 [b]
Carbon dioxide	36·1	7·2 [c]
Unidentified		9·4 [d]
Fission products		7·2 [e]

[a] Conversion of hexene 8·4 mole-%. [b] M 375; assumed to contain 4 hexene units. [c] $C_6H_{12} \longrightarrow 6\,CO_2$. [d] Estimate, based on analysis of liquid product recovered. [e] Estimate, based on hexene recovered, corresponds to overall fission reaction $C_6H_{12} \longrightarrow$ acraldehyde$+3CO_2$.

mechanism suggested by Twigg:[3] the essential feature of this is the addition of a hydroperoxy-radical to the olefinic double bond, followed by formation of an epoxide molecule and an alkoxy radical:



This scheme requires the formation of not more than 50% of epoxide from the olefin oxidised, as has been found previously [3-5] and again in the present case. The remaining 50% should turn up as products of further conversion of the alkoxy-radical; thus we find hexenyl propionate, hexenal, and hexenoic acid.

Twigg's suggested mechanism is further supported by Brill's work,[6a] particularly by his finding that mixtures of *cis*- and *trans*-2,3-epoxybutane are obtained when pure *cis*- or pure *trans*-but-2-ene, respectively, are oxidised.

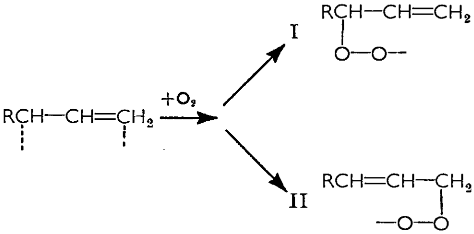
We have obtained clear support for Twigg's mechanism in experiments on the co-oxidation of cyclohexene and hex-1-ene. Cyclohexene oxidises about 20—30 times faster than hex-1-ene and, in the early stages of the reaction, the oxidation product is nearly exclusively cyclohexenyl hydroperoxide, only a negligible proportion of epoxycyclohexane being formed.

Thus in the co-oxidation of cyclohexene and hex-1-ene, the concentration of peroxy-radicals, should greatly exceed that in the oxidation of hex-1-ene alone. When hexene is present in large excess in a cyclohexene–hexene mixture these peroxyradicals should add to the hex-1-ene double bond rather than abstract a hydrogen atom from cyclohexene (Bolland mechanism) [1,2] if Twigg's mechanism operates, and a substantially increased yield of epoxide should result.

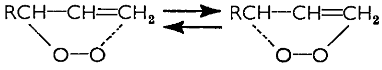
In co-oxidation experiments of cyclohexene with an excess of hexene, the yield of epoxide was in fact more than double that from an oxidation under the same conditions but with hexene alone. A blank experiment with cyclohexene confirmed that only a very small amount of epoxide was formed when hexene was absent.

Another interesting result is the production of derivatives of hex-2-ene only, derivatives of hex-1-ene not being detectable by the analytical methods described below. An isomerisation due to such a double-bond shift from hex-1-ene is to be expected in view of similar results recorded previously,[5] but the present extreme case of a practically complete change from primary to secondary olefinic structures seems exceptional.

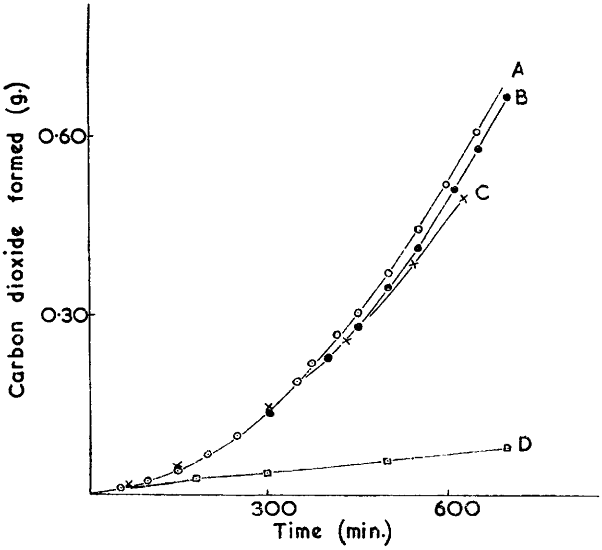
An explanation in terms of a preferred addition of oxygen to one of the two reactive positions of the allylic radical hybrid (a chain propagation step of the Bolland scheme) would require a ratio of about ten in the two rates. Such a ratio is not likely to arise because of differences in the entropies of activation; alternatively, it would correspond to a difference of 2—3 kcal./mole in the energies of activation. However, activation energies of radical additions to olefins are small and even in the present case, where they are increased through the loss of the delocalisation energy of the allyl radical, they should not exceed 5—10 kcal./mole; hence, a difference of 2—3 kcal./mole is improbable.



As an alternative explanation, it is suggested that a rapid interconversion of the two peroxy-radicals occurs *via* a five-membered transition state. If this leads to an equilibrium between the two isomeric radicals, the difference in the heats of formation will determine their relative stabilities and concentrations. Relevant data show that the bond dissociation energies of primary and secondary –C–O– bonds do not differ appreciably,[2,8] but a shift of the double bond from the C-1 to C-2 favours the latter by 2—3 kcal./mole.[9]



An allylic isomerisation of hydroperoxides is known in the steroid field, 3β-hydroxycholest-6-en-5α-yl hydroperoxide isomerising to 3β-hydroxycholest-5-en-7α-yl hydroperoxide.[10] Because the reaction is catalysed by peroxide and inhibited by phenols, it was concluded that a chain reaction involving the peroxy-radicals which correspond to the two hydroperoxides, occurs, by mechanism analogues to the one suggested here.



Formation of carbon dioxide in oxidation of hex-1-ene. A, B, Standard oxidation runs. C, Oxidation in chlorobenzene. D, Blank run. (Propionic acid without hex-1-ene.)

A final feature of the reaction is the extensive degradation to carbon dioxide, which

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[8] P. Gray and A. Williams, *Chem. Rev.*, 1959, **59**, 239.

[9] "Selected Values of Properties of Hydrocarbons," U.S. Nat. Bureau of Standards, Washington, 1947.

[10] G. O. Schenck, O. Albrecht Neumüller, and W. Eisfeld, *Annalen*, 1958, **618**, 202.

accounts for about 40% of the oxygen absorbed. Formation of carbon dioxide begins in the earliest stages of the reaction and continues at an increasing rate throughout, presumably because of the increasing concentration of precursors, which most likely are the aldehydes.[11-14]

EXPERIMENTAL

Apparatus and Procedure.—Reactions were carried out in a Pyrex vessel (25 cm. × 4·25 cm. internal diam.), heated in a glycerol bath controlled to ±0·5°. Dry oxygen was metered into the bottom of the vessel and left by a short water-cooled condenser and a solid carbon dioxide–acetone cold-finger, which returned the olefin and other materials to the vessel. The exit gases passed through a cold trap and through one of two U-tubes in parallel and containing " Carbosorb." The formation of carbon dioxide during the reaction was followed by weighing the tubes alternately.

The reaction conditions finally selected were 12 hr. at 80—85° with 25% w/w hex-1-ene (40 g.) in propionic acid plus 0·15—0·20% of cobalt propionate. A flow rate of 3·5—4·0 l./hr. of oxygen sufficed to stir the mixture. The solution was initially pink and slowly darkened during the reaction.

The oxidised mixture was neutralised with 20% sodium hydroxide solution. The hexene layer, roughly 90% of the hexene added, was washed with water to remove glycol (in the initial experiments), and dried ($MgSO_4$). Cobalt hydroxide was filtered off, and the solution extracted several times with ether until no further positive test for epoxide was obtained (test for glycol applied),[15] and the combined extracts were dried.

Vapour-phase chromatography on a silicone at 220° showed that both the ether and the hexene extracts contained essentially the same products but in different proportions. During identification of products the two solutions were worked up separately but, in later experiments, yields were obtained from the combined products after removal of solvent. The bulk of the solvent was removed at atmospheric pressure. The remaining solvent and the products were fractionated in small units at reduced pressures.

Analytical Methods.—Epoxide was determined by the method of Swern and his co-workers [16] or by the Malaprade reaction for glycols [17] after hydrolysis. Esters were analysed by semi-micro-scale hydrolyses [18] with 2·5M-sodium hydroxide in 90% methanol at 60°, followed by a glycol analysis for glycol esters and ester mixtures. The only carbonyl compound identified was hex-2-enal which was occasionally estimated with hydroxylamine hydrochloride, but more usually through its ultraviolet spectrum; a purified sample had a molar extinction coefficient of 20,300 ± 500 at $\lambda_{max.}$ = 216·0—216·5 mμ in n-hexane solution. Hydroperoxides were determined by the iodide–acetic acid method.

Materials.—*Hex-1-ene.* (L. Light and Co.). The fraction boiling between 63·7—63·9°/760 mm. was used (column of ten theoretical plates for this and similar preparations). The infrared spectrum fitted a reference curve accurately [19] and showed no trace of hex-2-ene.

Cyclohexene (B.D.H.). The fraction boiling between 82·5—82·7°/760 mm. was used.

Propionic acid (B.D.H.). The fraction boiling at 140·7—141·0°/760 mm. was used.

Cobalt propionate. Freshly prepared $CoCO_3,6H_2O$ was dissolved in a small excess of propionic acid, and the cobalt propionate precipitated with ether. Analysis of the dried product by e.d.t.a. gave Co, 28·7%. (Calc. for $C_6H_{10}CoO_4$: Co, 28·8%).

Hex-2-enal (L. Light and Co.). The fraction boiling at 69—70°/45 mm. was used.

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[11] (*a*) G. W. Ellis, *Biochem. J.*, 1936, **30**, 753; (*b*) N. I. Mitskevitch, T. I. Soroko, and M. M. Konoplyannik, *Sbornik Nauk Rabot. Inst. Fiz.-Org. Khim. Akad. Nauk Belorus. S.S.R.*, 1960, **8**, 175; T. I. Soroko, *ibid.*, p. 186.

[12] (*a*) D. H. Hey and W. A. Waters, *Chem. Rev.*, 1937, **21**, 169; (*b*) R. C. Hacman and A. Perrett, *Helv. Chim. Acta*, 1957, **40**, 2471.

[13] Emanuel, Nalbandyan, and Nieman, *Radioisotopes Sci. Res., Proc. Internat. Conf.*, Paris, 1957, **2**, 72.

[14] L. E. Gast, C. B. Coleman, and H. M. Teeter, *J. Org. Chem.*, 1959, **24**, 160.

[15] F. Feigl, " Spot Tests in Organic Analysis," Elsevier, London, 1956, 127.

[16] G. N. Billen, T. W. Findley, J. T. Scanlan, and D. Swern, *Analyt. Chem.*, 1947, **19**, 414.

[17] (*a*) L. Malaprade, *Bull. Soc. chim. France*, 1934, **1**, 833; (*b*) V. C. Mehlenbacher, " Organic Analysis," vol. 1, Interscience, New York, 1953, 41.

[18] A. M. Billmeyer, J. Mitchell, and D. M. Smith, *Analyt. Chem.*, 1952, **24**, 1847.

[19] " Documentation of Molecular Spectroscopy," Butterworth, London, 1959, No. 2784.

Hex-2-enoic acid (L. Light and Co.). Recrystallised from alcohol at −10° this had m. p. 32·0—32·5°.

Oxidation of Hex-1-ene Alone.—(a) *Typical fractions.* From 64 g. of hex-1-ene in a 12 hr. reaction: Fraction 1 (1·1 g.), b. p. up to 55°/30 mm.; 54% epoxide, 18% hexenal, and 15% hexenyl propionate. Fraction 3 (0·50 g.), b. p. 60—75°/12 mm.; 25% hexenal, 49% hexenyl propionate, and 9% glycol. Fraction 5 (1·6 g.), b. p. up to 120°/2 mm.; 49% glycol, 27% glycol dipropionate, 3% hexenal, plus a small amount of a possible hexenoate ester. Residue (0·90 g.), yellow-brown viscous liquid.

The small intermediate second and fourth fractions were examined by infrared spectroscopy to establish their main constituents by comparison with other fractions.

(b) *Identification of products.*—1,2-*Epoxyhexane.* In the 10—14 μ region the spectrum of the epoxide fitted exactly that of a synthetic specimen; no absorption peak corresponding to the 2,3-epoxide was detectable.[20]

Hex-2-enal. The material showed two absorption peaks, a strong one at 216—217 mμ and a weak one at 330—340 mμ, as found for a synthetic sample. The principal carbonyl frequency at 1695 cm.$^{-1}$, clearly indicated the C:C·C:O structure and was checked against a reference spectrum. The 2,4-dinitrophenylhydrazone had m. p. and mixed m. p. 144—145° (Found: C, 51·9; H, 5·1; N, 20·3. Calc. for $C_{12}H_{14}N_4O_4$: C, 51·8; H, 5·0; N, 20·1%); the semicarbazone had m. p. and mixed m. p. 169—170° (Found: C, 54·6; H, 8·0; N, 27·3. Calc. for $C_7H_{13}N_4O$: C, 54·2; H, 8·4; N, 27·1%).

Hexane-1,2-diol. This was identified through its 1-naphthylurethane, m. p. 142—143° (Found: C, 73·6; H, 6·3; N, 6·0. Calc. for $C_{28}H_{28}N_2O_4$: C, 73·7; H, 6·2; N, 6·1%). Two melting points have been recorded for this derivative, 155—160° and 172—174°, after synthesis by two methods.[21] The identity of the glycol was confirmed by a test-tube oxidation with sodium bismuthate, the resulting solution giving a strong positive reaction for formaldehyde with chromotropic acid, confirming the presence of a 1,2-glycol.

Hexanediol dipropionate. A final fraction obtained from the hexene layer, and freed from glycol showed strong peaks at 1730 and 1190 cm.$^{-1}$, characteristic of esters (Found: C, 63·1; H, 9·2. Calc. for $C_{12}H_{22}O_4$: C, 62·6; H, 9·6%). Quantitative hydrolysis indicated 82·5 ± 1% of hexanediol dipropionate and subsequent glycol determination gave 83 ± 2%. The 1-naphthylurethane of the glycol obtained on aqueous hydrolysis again had m. p. 142° (Found: C, 73·6; H, 6·4; N, 5·9%).

Hex-2-enyl propionate. The middle fraction (and others), contained a large amount of an ester that was not derived from a glycol (spectral absorption at 1726 and 1190 cm.$^{-1}$). Quantitative hydrolysis indicated 48% of hexenyl propionate, and glycol analysis before and after gave 9 ± 1%. The 1-naphthylurethane had m. p. 78—80° (Found: C, 75·5; H, 7·5; N, 5·0. Calc. for $C_{17}H_{29}NO_2$: C, 75·8; H, 7·1; N, 5·2%). The m. p. of the hex-2-en-1-ol derivative is [22] as 76°; that of hex-1-en-3-ol is not known. The *S*-benzylthiuronium salt, m. p. and mixed m. p. 147°, of the acid was identified as that of propionic acid. It can be reasonably concluded that this ester is largely hex-2-enyl propionate.

Hex-2-enoic acid. This was the only acid detectable in a large excess of propionic acid by means of its ultraviolet spectrum ($\lambda_{max.}$ = 212—214 mμ, molecular extinction coefficient 8000—11,000 in water). Because of several uncertainties (extinction coefficient, solution composition), ultraviolet analysis of the aqueous solution after removal of the nonacidic products was considered to be accurate to about 10% only. With this procedure, 0·9 g. of hexenoic acid were detected as product in a reaction of 42 g. of hex-1-ene. A little of the material was extracted as a strongly acid, dark oil which could not be crystallised. The *S*-benzylthiuronium salt had m. p. and mixed m. p. 163° (Found: C, 60·3; H, 7·0; N, 10·2. Calc. for $C_{14}H_{19}N_2O_2S$: C, 60·3; H, 6·8; N, 10·0%).

Residue. The residue (*M*, 350—400) was neutral, not hydrolysed by alkali, and saturated (no reaction with bromine), but gave a positive test for aldehyde with tetrazolium salt solution. The infrared spectrum shows a saturated carbonyl absorption peak at 1715 cm.$^{-1}$ and a peak at 1110 cm.$^{-1}$, which may indicate an ether link.

Other possible products. (i) *Hex-1-en-3-ol and hex-1-en-3-one.* The occurrence or absence

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[20] Belfitt, Ph.D. Thesis, Pennsylvania State Univ., 1957, Microfilm No. 20949.

[21] P. A. Levene and H. L. Haller, *J. Biol. Chem.*, 1928, **79**, 483.

[22] I. Heilbron and H. M. Bunbury, " Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953.

of these products was important. The common feature is the terminal vinyl group which would have characteristic absorption peaks at 905—915 and 985—995 cm.$^{-1}$. Bands at these frequencies were not detectable in the spectrum of any product (the region was somewhat masked by large amounts of epoxide), but the corresponding single band of hexenal was clearly visible at 976 cm.$^{-1}$. The unsaturated carbonyl frequency at 1695 cm.$^{-1}$ was not resolved into more than one peak by a Perkin-Elmer 21 instrument nor could the 2,4-dinitrophenylhydrazone obtained from the products be separated into more than one material. Compounds containing the carbon skeleton C·C·C·C·C:C therefore form only a minor fraction of the products.

(ii) *Minor products.* The presence of several unidentified minor products was revealed by small peaks in the vapour-phase chromatogram. The total quantity of unidentified product was estimated from the quantity and analysis of liquid product recovered.

(iii) *Fission products.* The comparatively large amount of carbon dioxide formed indicates that short-chain aldehydes and acids ought to be present, but they were not detectable in the presence of a large excess of propionic acid; this is a limitation of the present method of reaction. On the other hand, this method traps radicals as esters of the acid solvent and thus reduces degradation of the oxidation product. An estimate of the quantity of fission products based on hexene recovered shows that it corresponded approximately to an overall fission reaction $C_6H_{12} \longrightarrow$ acraldehyde + $3CO_2$. Traces of acraldehyde were identified in the exhaust gases.

*Isomerisation of hex-*1*-ene.* Although isomerisation to hex-2-ene was unlikely under the conditions used, on two occasions samples of the recovered hexene were examined unsuccessfully for hex-2-ene (infrared absorption peaks at 863 and 986 cm.$^{-1}$); a few per-cent of hex-2-ene would have been detectable.

(c) *Yields.* Yields are given in Table 1 and are believed to be reproducible to $\pm 10\%$.

*Oxidation of Cyclohexene–Hex-*1*-ene Mixtures.*—Three experiments were needed to examine the effects of the addition of cyclohexene on the yields of epoxide in hex-1-ene oxidation: (1) a standard oxidation of hex-1-ene, (2) a similar oxidation with the addition of cyclohexene, and (3) a blank experiment without hex-1-ene. In experiments (1) and (2) 40 g. of hex-1-ene were used; in (2) and (3) about 0·5 g. of cyclohexene (in propionic acid) was added per hour, beginning after 1 hr., until 4·75 g. had been added in all; the reaction was then continued for a further 100 min.

The information required was the total epoxide yield in each experiment. Since the epoxide does not remain unchanged but is partly converted into glycol and again into glycol esters (in this case), the total epoxide plus glycol had to be determined. Additional wastage of epoxide may occur by other reactions, *e.g.*, by rearrangement to aldehydes, but likely products of such reactions were not observed. The reaction mixture was worked up normally and a weighed quantity of the total product after careful removal of the solvent was quantitatively hydrolysed by the semimicro-procedure. The resulting solution contained all the epoxide product as glycol and was analysed accordingly. Yields were (1) 0·91 (2) 2·25 (3) *ca.* 0·10 g. of epoxide.

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