Mechanisms of Antioxidant Action. Part 4.[1] The Decomposition of 1-Methyl-1-Phenylethyl Hydroperoxide by Zinc Dialkyldithiocarbamates and Zinc Xanthates

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Four zinc dithiocarbamates and two zinc xanthates have been used as promoters for the decomposition of 1-methyl-1-phenylethyl hydroperoxide (cumene hydroperoxide). The distribution of products formed from the hydroperoxide is independent of the promoter. This, together with other evidence in the literature, suggests that the dithiocarbamates and xanthates decompose the hydroperoxide *via* the formation of sulphur trioxide–sulphuric acid. This is in direct contrast to the results obtained in previous work using zinc *O,O′*-dialkyl(aryl)phosphorodithioates (zinc DDPs) as promoters where the hydroperoxide decomposition catalyst was shown to be the corresponding acid *O,O′*-dialkyl(aryl) hydrogen phosphorodithioate.

In two previous papers[1,2] results were reported for the decomposition of 1-methyl-1-phenylethyl hydroperoxide (cumene hydroperoxide) promoted by a range of metal *O,O′*-dialkyl(aryl)phosphorodithioates (**1**).† The experimental evidence was consistent with a mechanism of hydroperoxide decomposition in which: (a) acetophenone was formed from the hydroperoxide *via* a free radical reaction which was independent of the promoter; (b) 2-phenylpropan-2-ol (alcohol), 2-phenylpropene (propene), phenol, and propan-2-one were formed *via* ionic decomposition of the hydroperoxide; and (c) the metal DDPs formed the corresponding DDP acid (**2**) which was the catalyst for hydroperoxide decomposition, initiating an ionic chain reaction by protonating both oxygen atoms of the hydroperoxide.

$[(RO)_2PS_2]_xM_y$ (**1**)

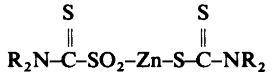
a; M = Co, $x = 2, y = 1$
b; M = Ni, $x = 2, y = 1$
c; M = Cu, $x = 4, y = 4$
d; M = Zn, $x = 2, y = 1$

$(RO)_2PS_2H$ (**2**)

$[(RO)_2PS_2]_2$ (**3**)

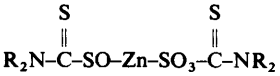
$(XCS_2)_2Zn$ (**4**)

a; X = $(C_2H_5)_2N$
b; X = $(n\text{-}C_4H_9)_2N$
c; X = $C_5H_{10}N$
d; X = $(C_6H_5CH_2)_2N$
e; X = C_2H_5O
f; X = $i\text{-}C_3H_7O$



$R_2N\text{-}\overset{\overset{S}{\|}}{C}\text{-}SO_2\text{-}Zn\text{-}S\text{-}\overset{\overset{S}{\|}}{C}\text{-}NR_2$

(**5**)



$R_2N\text{-}\overset{\overset{S}{\|}}{C}\text{-}SO\text{-}Zn\text{-}SO_3\text{-}\overset{\overset{S}{\|}}{C}\text{-}NR_2$

(**6**)

There have been other suggestions for the hydroperoxide decomposition catalyst formed from metal DDPs. In particular Okhatsu *et al.*[3–5] have suggested that the catalyst, formed from zinc DDPs, is sulphuric acid obtained by oxidation of the DDP ligand. Similarly, Al-Malaika and co-workers[6–8] have suggested that the catalyst formed from a nickel DDP is sulphur trioxide–sulphuric acid formed by oxidation of the DDP ligand *via* an intermediate disulphide (**3**) and sulphur dioxide. In proposing their mechanism for the formation of sulphuric acid Al-Malaika and co-workers suggest that the nickel DDP is similar to nickel dithiocarbamates and nickel xanthates which are also assumed to decompose hydroperoxides *via* the formation of sulphur dioxide followed by oxidation to sulphur trioxide. There is good evidence that sulphur dioxide is implicated in the mechanism of hydroperoxide decomposition promoted by zinc dithiocarbamates since the dithiocarbamate reacts with hydroperoxides to form sulphur dioxide.[9] Zinc DDPs do not, however, react with hydroperoxides to evolve sulphur dioxide.[10,11] This simple difference has led to criticism of the idea that sulphur dioxide is involved in the decomposition of hydroperoxides promoted by metal DDPs.[1]

The purpose of this paper is to attempt to clarify the situation. Four zinc dithiocarbamates (**4a**—**d**) and two zinc xanthates (**4e** and **f**) have been used as promoters for the decomposition of cumene hydroperoxide. The experimental conditions used were as similar as possible to the conditions used in previous work[2] when zinc DDPs were used as promoters for the decomposition of cumene hydroperoxide. Thus comparison of the results in this paper with the previous results for zinc DDPs allows a fair comparison between the different dithioate complexes as promoters for hydroperoxide decomposition.

Experimental

The solvents used in this study were AnalaR grade. The zinc dithiocarbamates and the isopropyl zinc xanthate (**4f**) were purchased materials (Robinson Brothers Ltd.). The ethyl zinc xanthate (**4e**) was made by a metathetical reaction using aqueous solutions of ethyl potassium xanthate and zinc sulphate. All the compounds were recrystallised before use and characterised by elemental analysis, melting points, and i.r. spectroscopy. Cumene hydroperoxide was purified *via* its sodium salt and its purity checked by iodometric titration[12] and h.p.l.c. (>99%).

Details of the kinetic experiments have been given previously.[2] Briefly, the decomposition of cumene hydroperoxide in n-decane is carried out under nitrogen and small samples of

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† For the sake of brevity *O,O′*-dialkyl(aryl)phosphorodithioate will be abbreviated to DDP, so the zinc complexes will be referred to as zinc DDPs.

Table 1. Product distribution (%) of the decomposition of cumene hydroperoxide promoted by zinc dithiocarbamates and zinc xanthates. $[\text{Promoter}]_0 = [\text{S}]_0 = 1.20 \times 10^{-4}$ mol dm^{-3}; $[\text{RO}_2\text{H}]_0 = 7.0 \times 10^{-2}$ mol dm^{-3}; temperature = 383 ± 0.1 K

Promoter	[Phenol]	[Alcohol + propene]	[Acetophenone]	Yield
(4a)	76.0 ± 2.5	20.1 ± 2.4	3.86 ± 0.66	94.9
(4b)	74.6 ± 2.2	21.8 ± 1.7	3.57 ± 0.53	94.6
(4c)	76.9 ± 3.1	19.3 ± 2.7	3.74 ± 0.72	95.8
(4d)	76.3 ± 2.6	19.8 ± 2.1	3.89 ± 0.82	96.6
(4e)	77.0 ± 2.6	19.5 ± 2.1	3.53 ± 0.77	93.9
(4f)	74.6 ± 3.7	21.9 ± 3.6	3.51 ± 0.28	94.7

Table 2. Activation parameters for the decomposition of cumene hydroperoxide promoted by zinc dithiocarbamates and xanthates. $[\text{Promoter}]_0 = [\text{S}]_0 = 1.20 \times 10^{-4}$ mol dm^{-3}; $[\text{RO}_2\text{H}]_0 = 7.0 \times 10^{-2}$ mol dm^{-3}

Promoter	E^*/kJ mol^{-1}	ln (A/h^{-1})	ΔH^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}
(4a)	144.1 ± 9.6	44.6 ± 3.0	141.0 ± 9.6	48 ± 25
(4b)	277.4 ± 23.3	86.8 ± 7.4	274.2 ± 23.3	398 ± 62
(4c)	325.1 ± 22.4	99.7 ± 7.0	321.8 ± 22.4	506 ± 58
(4d)	179.3 ± 6.5	56.5 ± 2.1	176.1 ± 6.5	147 ± 17
(4e)	93.1 ± 10.4	28.0 ± 3.3	90.0 ± 10.5	-91 ± 28
(4f)	298.1 ± 17.2	91.0 ± 5.4	294.9 ± 17.2	433 ± 45

the reaction mixture are removed every 30 min for analysis. The samples are analysed using h.p.l.c. to determine the concentration of 2-phenylpropene, acetophenone, cumene hydroperoxide, phenol, and 2-phenylpropan-2-ol. No attempt is made to analyse for propan-2-one because of the high temperatures used. The formulae for calculating the percentage yield of the products and the distribution of the products are given in the previous paper.

The rate constants were calculated using standard methods of linear regression analysis. The correlation coefficient (r) of the regression analysis was used to calculate the Students t-parameter and this parameter was used to test the null hypothesis (H_0; $r = 0$) against the alternate hypothesis (H_0; $r \neq 0$).[12] The null hypothesis was rejected if $P > 99.99\%$. Reactions followed to *ca.* three half-lives showed no significant deviation from linearity and duplicate experiments showed that the rate constants were reproducible to $\pm(6—10)\%$. Product distributions were compared using a two-tailed Student's t-test or variance analysis, and the null hypothesis (H_0; $\mu_1 = \mu_2 =$ *etc.*) was rejected if $P > 95\%$. Throughout this paper the errors quoted are standard deviations.

Results and Discussion

Distribution of Products formed from Cumene Hydroperoxide.—In the previous work[2] using zinc DDPs as promoters for the decomposition of cumene hydroperoxide the distribution of products formed from the hydroperoxide was measured at a temperature of 383.0 ± 0.1 K with constant initial concentrations of the hydroperoxide ($[\text{RO}_2\text{H}]_0 = 7.0 \times 10^{-2}$ mol dm^{-3}) and the promoter ($[\text{promoter}]_0 = [\text{S}]_0 = 30.0 \times 10^{-6}$ mol dm^{-3}, where $[\text{S}]_0$ is the original concentration of sulphur). Some preliminary experiments were carried out using the zinc dithiocarbamates and zinc xanthates under the same experimental conditions. However, the rate of hydroperoxide decomposition was found to be too slow for convenient measurement. Thus experiments with the zinc dithiocarbamates and zinc xanthates have been carried out using a higher initial concentration of the promoter ($[\text{promoter}]_0 = [\text{S}]_0 = 1.20 \times 10^{-4}$ mol dm^{-3}).

The product distributions and yields formed from the decomposition of cumene hydroperoxide promoted by the zinc dithiocarbamates and zinc xanthates are shown in Table 1. Variance analysis of the results shows that there are no significant differences in the levels of phenol, acetophenone, and (alcohol + propene) so that all the product distributions are, in effect, identical. This suggests that all the zinc dithiocarbamates and zinc xanthates tested decompose the hydroperoxide *via* the same catalyst. In contrast, the product distributions obtained from the decomposition of cumene hydroperoxide promoted by the zinc DDPs showed significant differences in the levels of phenol and (alcohol + propene) that were formed, implying that different catalysts were formed from each zinc DDP.

Activation Parameters for the Decomposition of Cumene Hydroperoxide.—In the temperature range 368—398 K the zinc dithiocarbamates and zinc xanthates promoted the decomposition of cumene hydroperoxide in a reaction that was second order with respect to the hydroperoxide. The activation parameters are shown in Table 2 and are corrected to allow for the difference in dimensions between the rate constant (k_2) and the Eyring equation, which is only applicable to first-order rate constants.[13,14]

Despite the fact that the product distributions are identical for the range of promoters used, the activation parameters cover a wide range of values. There is an isokinetic relationship between ΔH^* and ΔS^* which can be represented by equation (1).

$$\Delta H^* = (390.2 \pm 6.6)\,\Delta S^* + (122.6 \pm 2.2) \times 10^3 \quad (1)$$

Activation Parameters for the Formation of the Decomposition Products from Cumene Hydroperoxide.—The activation parameters for the formation of acetophenone, 2-phenylpropene, and phenol have been calculated. In each case the rate of formation of the decomposition products was second order with respect to the hydroperoxide and the activation parameters have been corrected as before.

Variance analysis of the plots of ln k against $1/T$ shows that the activation parameters for the formation of acetophenone are independent of the promoter and are similar to values obtained for the free-radical decomposition of cumene hydroperoxide[15-17] and the activation parameters for the formation of acetophenone in cumene hydroperoxide decompositions promoted by metal DDPs.[1,2] These results suggest that in the decomposition of cumene hydroperoxide promoted by metal DDPs, zinc dithiocarbamates, and zinc xanthates the formation of acetophenone is a free-radical reaction that is independent of the promoter.

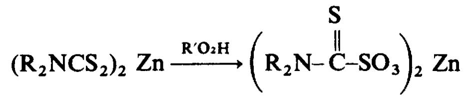
Variance analysis of the plots of ln k against $1/T$ shows that the activation parameters for the formation of 2-phenylpropene are independent of the promoter and are not significantly different from previous results for cumene hydroperoxide decompositions promoted by metal DDPs.[1,2] Furthermore, the activation parameters are similar to results obtained for the acid-catalysed dehydration of 2-phenylpropan-2-ol to 2-phenylpropene.[18–20] Also, in the decomposition of cumene hydroperoxide promoted by the zinc dithiocarbamates and zinc xanthates the amount of 2-phenylpropan-2-ol formed was small and constant suggesting that the alcohol is an intermediate in the decomposition of cumene hydroperoxide to form 2-phenylpropene. These results suggest that in the decomposition of cumene hydroperoxide promoted by the zinc dithiocarbamates and zinc xanthates the activation parameters for the formation of (alcohol + propene) cannot be determined because the kinetics are dominated by a secondary reaction, the dehydration of the alcohol to the propene.

There are significant differences between the activation parameters for the formation of phenol by the different promoters and this can be formally verified using variance analysis. There is also an isokinetic relationship between the values of ΔH^* and ΔS^* [equation (2)] and variance analysis shows that there is no significant difference between this regression line and the comparable line for the decomposition of cumene hydroperoxide [equation (1)]. Thus, if the existence

$$\Delta H^* = (389.2 \pm 7.3)\,\Delta S^* + (128.3 \pm 1.1) \times 10^3 \quad (2)$$

of an isokinetic relationship is indicative of a common reaction mechanism[21,22] it follows that the mechanism for the formation of phenol is the same as the mechanism of decomposition of the hydroperoxide. Therefore, since phenol is formed from cumene hydroperoxide by an ionic mechanism, it follows that the results in Table 2 are the activation parameters for the over-all rate of ionic decomposition of the hydroperoxide

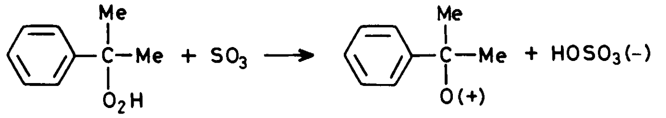
Relationship between these Results and Previous Work.—In 1964 it was established that zinc dithiocarbamates[9] and zinc xanthates[23] promote the decomposition of hydroperoxides. These early observations have been confirmed by a number of workers[6,8,24–27] not only for the zinc complexes but also for nickel and other transition metal dithiocarbamates and xanthates. In their work Holdsworth *et al.*[9] established that a zinc dithiocarbamate reacts with a hydroperoxide to form sulphur dioxide. Thus the zinc dithiocarbamate is similar to dilaurylthiodipropionate,[28] aryl sulphides,[29] thiophenes,[30] and zinc mercaptobenzothiazole,[8,31] which also react with hydroperoxides to form thermally unstable compounds that evolve sulphur dioxide. It is assumed[8,24,25,32] that sulphur dioxide is formed from a zinc dithiocarbamate by oxidation of the ligand and decomposition of the resulting complex [equation (3)].



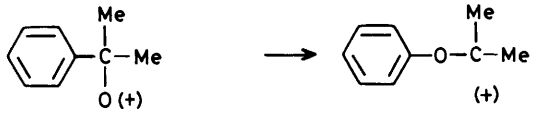
$$(R_2NCS_2)_2\,Zn \xrightarrow{R'O_2H} \left(R_2N\text{-}\overset{\overset{\displaystyle S}{\|}}{C}\text{-}SO_3\right)_2 Zn \quad (3)$$

This assumption is based upon the early work of Brooks[33] who isolated complexes (5) and (6). It should be pointed out, however, that these complexes were not formed by direct oxidation of the corresponding zinc dithiocarbamate and did not thermally decompose to form sulphur oxides. Hence the exact mechanism for the formation of sulphur oxides from the reaction of zinc dithiocarbamates with hydroperoxides is not established.

Since small quantities of sulphur dioxide promote the decomposition of hydroperoxides[9,29,34,35] it was natural to assume that sulphur dioxide was the catalyst for hydroperoxide decomposition. Recent work by Husbands and Scott[36] shows that sulphur dioxide is oxidised by hydroperoxide to sulphur trioxide and that this reaction precedes the catalytic decomposition of the hydroperoxide. Husbands and Scott proposed that sulphur trioxide catalyses the decomposition of hydroperoxides by acting as a Lewis acid [*e.g.*, equations (4)—(6)].



(4)



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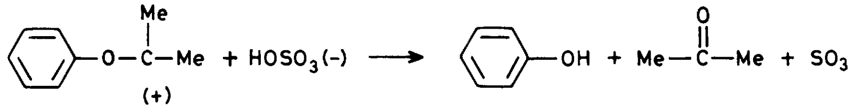

(6)

Alternatively, the sulphur trioxide could scavenge traces of water to form sulphuric acid, which catalyses the decomposition of hydroperoxides by protonating the hydroperoxide. The mechanism would then be similar to that proposed for the decomposition of cumene hydroperoxide catalysed by *O,O'*-dialkyl hydrogen phosphorodithioates (Scheme).[1,2] The kinetics we observe for the composition of cumene hydroperoxide promoted by zinc dithiocarbamates and zinc xanthates are consistent with the sulphur trioxide scavenging water to form sulphuric acid. As we have seen before[2] the proposed reaction scheme for the acid-catalysed decomposition of cumene hydroperoxide will give second-order kinetics [equation (7)] if the concentration of water in the system is small.

$$\frac{1}{[RO_2H]_t} - \frac{1}{[RO_2H]_0} \simeq \frac{K_1K_2k_5k_7[H^+]t}{k_6[H_2O]} \quad (7)$$

$$RO_2H + H^+ \rightleftharpoons RO_2H_2^+ \qquad (K_1)$$

$$RO_2H_2^+ \rightleftharpoons R\text{-}\underset{H}{\overset{(+)}{O}}\text{-}OH \qquad (K_2)$$

$$RO_2H_2^+ \longrightarrow RO^+ + H_2O \qquad (k_3)$$

$$RO^+ \longrightarrow C^+ \qquad (k_4)$$

$$C^+ + RO_2H \longrightarrow \text{Phenol} + \text{propan-2-one} + RO^+ \qquad (k_5)$$

$$C^+ + H_2O \longrightarrow \text{Phenol} + \text{propan-2-one} + H^+ \qquad (k_6)$$

$$R\text{-}\underset{H}{\overset{(+)}{O}}\text{-}OH \longrightarrow R^+ + H_2O_2 \qquad (k_7)$$

$$R^+ + RO_2H \longrightarrow ROH + RO^+ \qquad (k_8)$$

$$ROH \xrightarrow{H+} \text{2-Phenylpropene} + H_2O \qquad (k_9)$$

Scheme.

The evidence discussed, so far, is thus consistent with the idea that sulphides (alkyl, aryl, and heterocyclic) and zinc mercaptobenzothiazole and dithiocarbamates react with hydroperoxides to form thermally unstable compounds that evolve sulphur dioxide. The sulphur dioxide is further oxidised to sulphur trioxide–sulphuric acid which catalyses the decomposition of the hydroperoxide. It is tempting to add metal DDPs to this scheme and to assume that they also react with hydroperoxides to form sulphur trioxide. There are, however, significant differences between the decomposition of cumene hydroperoxide promoted by metal DDPs and the decomposition of cumene hydroperoxide promoted by zinc dithiocarbamates and zinc xanthates. These differences, highlighted by the work reported in this paper and the previous results using zinc DDPs,[2] show that the hydroperoxide decomposition catalyst formed from zinc DDPs is probably different from the catalyst formed from the zinc dithiocarbamates and xanthates. The argument supporting this conclusion is as follows.

(*i*) When a metal DDP is reacted with a hydroperoxide no sulphur dioxide is evolved.[10,11]

(*ii*) The rate of hydroperoxide decomposition promoted by a metal dithiocarbamate or metal xanthate is significantly slower than the rate of decomposition promoted by a metal DDP. This was demonstrated by Al-Malaika and co-workers[6–8] using nickel complexes and has been confirmed for zinc complexes by the results reported in this paper. Thus if sulphur oxides are the catalyst formed from metal dithiocarbamates, xanthates, and DDPs it follows that the rate of formation of sulphur oxides formed from the metal DDPs will have to be greater than the rate of formation of sulphur oxides from metal dithiocarbamates and xanthates. Yet no sulphur dioxide can be detected in the reaction of zinc DDPs with hydroperoxides.

(*iii*) When zinc dithiocarbamates and xanthates are used to promote the decomposition of cumene hydroperoxide there are no significant differences in the product distributions obtained. This suggests that the same catalyst is formed from these promoters which is entirely consistent with the idea that the catalyst is sulphur trioxide. In contrast, when the zinc DDPs are used to promote the decomposition of cumene hydroperoxide the product distribution depends upon the zinc DDP used. This suggests that different catalysts are formed from each zinc DDP.

(*iv*) It cannot be argued that for the zinc DDP-promoted decompositions the differences in product distribution result from the zinc DDPs forming different concentrations of the same catalyst. The activation parameters reported in this paper for the hydroperoxide decompositions promoted by zinc dithiocarbamates and zinc xanthates show quite clearly that the *rate* of hydroperoxide decomposition depends upon the promoter used but the product distribution is unaffected.

The product distribution depends upon the relative magnitudes of K_1 and K_2 (Scheme) since protonation of the α-oxygen atom of the hydroperoxide leads to the formation of phenol and acetone while protonation at the β-oxygen atom leads to the formation of 2-phenylpropan-2-ol and 2-phenylpropene. The relative magnitude of K_1 and K_2 depends upon the acid being used but will be constant for a given acid at a given temperature. Hence a range of promoters, producing the same acid catalyst, will yield the same product distribution when compared at the same temperature.

The rate of hydroperoxide decomposition depends not only upon K_1 and K_2 but also upon the amount of acid formed [equation (7)] and this will affect the activation parameters for the over-all rate of decomposition of the hydroperoxide. Hence, if we assume that the dithocarbamates and xanthates form sulphur trioxide–sulphuric acid at different rates it is possible to have a range of promoters that give the same product distribution but different rates of reaction.

Thus if we assume that zinc dithiocarbamates and xanthates decompose cumene hydroperoxide *via* the formation of sulphur trioxide–sulphuric acid (and all the evidence is consistent with this assumption) it is clear that another catalyst(s) is involved in the decomposition of cumene hydroperoxide promoted by zinc DDPs. The evidence presented in the previous paper[2] is consistent with the assumption that zinc DDPs form the corresponding acid (**2**), which is the hydroperoxide catalyst.

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References

1 Part 3, M. D. Sexton, *J. Chem. Soc., Perkin Trans. 2*, in the press, (4/116).
2 A. J. Bridgewater, J. R. Dever, and M. D. Sexton, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1006.
3 Y. Okhatsu, H. Ueda, K. Kikkawa, and T. Osa, *Yukagaku*, 1977, **26**, 296.
4 Y. Okhatsu, K. Kikkawa, and T. Osa, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3606.
5 Y. Okhatsu, *Junkatsu*, 1978, **23**, 606.
6 S. Al-Malaika and G. Scott, *Eur. Polym. J.*, 1980, **16**, 503.
7 S. Al-Malaika and G. Scott, *Polymer*, 1982, **23**, 711.
8 S. Al-Malaika, K. B. Chakraborty, and G. Scott, in 'Developments in Polymer Stabilisation,' ed. G. Scott, Applied Science, London, 1983, vol. 6, p. 73.
9 J. D. Holdsworth, G. Scott, and D. Williams, *J. Chem. Soc.*, 1964, 4692.
10 A. J. Burn, R. Cecil, and V. O. Young, *J. Inst. Pet., London*, 1971, **57**, 319.
11 M. D. Sexton, unpublished work.
12 R. D. Mair and A. J. Graupner, *Anal. Chem.*, 1964, **38**, 194.
13 R. K. Boyd, *J. Chem. Educ.*, 1978, **55**, 84.
14 P. J. Robinson, *J. Chem. Educ.*, 1978, **55**, 509.
15 J. R. Thomas, *J. Am. Chem. Soc.*, 1955, **77**, 246.

16 G. H. Twigg, G. W. Yodin, H. C. Bailey, and J. Holden, *Erdoel Kohle*, 1962, **15**, 74.
17 V. L. Antonovskii, E. T. Denisov, and L. V. Solntseva, *Kinet. Katal.*, 1965, **8**, 815.
18 W. M. Shubert and B. Lamm, *J. Am. Chem. Soc.*, 1966, **88**, 120.
19 J. P. Durand, M. Davidson, M. Hellin, and F. Coussemont, *Bull. Soc. Chim. Fr.*, 1966, **43**, 52.
20 J. L. Jensen and D. J. Carre, *J. Org. Chem.*, 1971, **36**, 3180.
21 O. Exner, *Prog. Phys. Org. Chem.*, 1973, **10**, 411, and references cited therein.
22 R. R. Krug, W. G. Hunter, and R. G. Greiger, *J. Phys. Chem.*, 1976, **80**, 2335, 2341, and references cited therein.
23 T. Colclough and J. I. Cunneen, *J. Chem. Soc.*, 1964, 4790.
24 G. Scott, *Rev. Sulphur Chem.*, 1969, **4**, 99.
25 G. Scott, *Br. Polym. J.*, 1971, **3**, 23.
26 P. I. Sanin, V. V. Sher, I. V. Shkhiyants, and G. N. Kuzmina, *Neftekhimiya*, 1978, **18**, 693.
27 R. P. R. Ranaweera and G. Scott, *Eur. Polym. J.*, 1976, **12**, 825.
28 N. P. Neureiter and D. E. Bown, *Ind. Eng. Chem., Prod. Res. Dev.*, 1962, **1**, 236.
29 A. J. Bridgewater and M. D. Sexton, *J. Chem. Soc., Perkin Trans. 2*, 1978, 530.
30 W. J. M. van Tilborg and P. Smael, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 132.
31 M. J. Husbands and G. Scott, *Eur. Polym. J.*, 1979, **15**, 879.
32 G. Scott, *Chem. Br.*, 1973, **9**, 267.
33 L. A. Brooks, *Rubber Chem. Technol.*, 1963, **36**, 887.
34 J. C. W. Chien and C. R. Boss, *J. Polym. Sci.. A-1*, 1972, **10**, 1579.
35 J. P. Fortuin and H. I. Waterman, *Chem. Eng. Sci.*, 1953, **2**, 182.
36 M. J. Husbands and G. Scott, *Eur. Polym. J.*, 1979, **15**, 249.

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