Kinetic and Thermodynamic Control of the Ratio of Markownikoff to anti-Markownikoff Addition

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ELECTROPHILIC additions to conjugated dienes give predominantly 1,2-addition when the products are kinetically controlled, but give largely the 1,4-adduct when the products are thermodynamically controlled.[1] An example of an analogous change in the products of an electrophilic addition to an alkene from predominantly anti-Markownikoff to largely Markownikoff in orientation due to kinetic or thermodynamic control has not, to our knowledge, been previously reported.

The addition of 2,4-dinitrobenzenesulphenyl chloride to 3,3-dimethylbut-1-ene in acetic acid solution at 25° gives predominantly the anti-Markownikoff adduct, 1-chloromethyl-2,2-dimethylpropyl 2,4-dinitrophenyl sulphide (I) together with the Markownikoff adduct, 2-chloro-3,3-dimethylbutyl 2,4-dinitrophenyl sulphide (II), and a mixture of isomeric acetates (III) At higher temperatures a further product 1-(2,4-dinitrophenylthio)-2,3-dimethylbut-2-ene (IV) is obtained. Previous work[2] has shown that the arylsulphur moiety is the electrophilic portion of the reagent. The proportions of the different products varied with the temperature and with the time of reaction as shown in the Table. At all temperatures the total yield of product was over 90%.

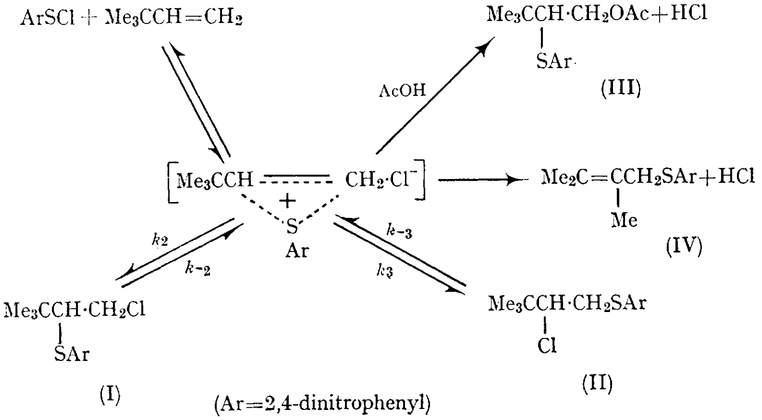
TABLE

Percentage of each product at various temperatures and times of reaction

Temperature	25°	100	100	100	118·5	118·5
Time	2 days	15 min.	60 min.	180 min.	15 min.	180 min.
% (I)	94	84	65	50	80	4
% (II)	4	9	19	37	14	63
% (III)	1	4	9	8	5	29
% (IV)	—	3	8	6	—	4

At 25° the chlorosulphides (I) and (II) were stable in acetic acid solution; at 100° either isomer gave an equilibrium mixture of the chlorosulphides containing 98% of the Markownikoff adduct (II) together with the mixture of acetates (III) and the unsaturated sulphide (IV). Equilibrium was attained in about 5 days. The rate of disappearance of the thermodynamically less stable anti-Markownikoff adduct (I) was first-order up to 60% reaction, the velocity constant being $3{\cdot}3 \times 10^{-5}$ sec.$^{-1}$ The magnitude of this velocity constant is such that the higher yield of the Markownikoff adduct (II) obtained with longer reaction times at 100° must have arisen from an anionotropic rearrangement of the anti-Markownikoff adduct (I).

These results may be explained on the basis of the mechanism:



in which $k_{-2} > k_{-3}$, and for steric reasons[3] $k_2 > k_3$. The free energies of activation for the product-forming steps will be lower than those for the reverse reactions. This will result in kinetic control giving anti-Markownikoff addition at lower temperatures, and with short reaction times, but thermodynamic control giving the Markownikoff adduct at higher temperatures with high reaction times. This unusual behaviour is presumably due to the branched structure of the alkene, and the mobility of the anion caused by the relative stability of the episulphonium ion intermediate.

The products were separated by thin-layer chromatography, and determined spectrophotometrically. The structures of the chlorosulphides were established by conversion into corresponding unsaturated sulphones, which were identified by their n.m.r. spectra.

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[1] C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, New York, 1953, p. 653.

[2] W. L. Orr and N. Kharasch, *J. Amer. Chem. Soc.*, 1953, **75**, 6030; 1956, **78**, 1201.

[3] W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, 1957, **79**, 3469.