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FREE RADICAL ADDITIONS. PART VII 1). FREE RADICAL ADDITION OF BROMOMALONONITRILE TO ALKENES; RELATIVE RATE CONSTANTS ++)

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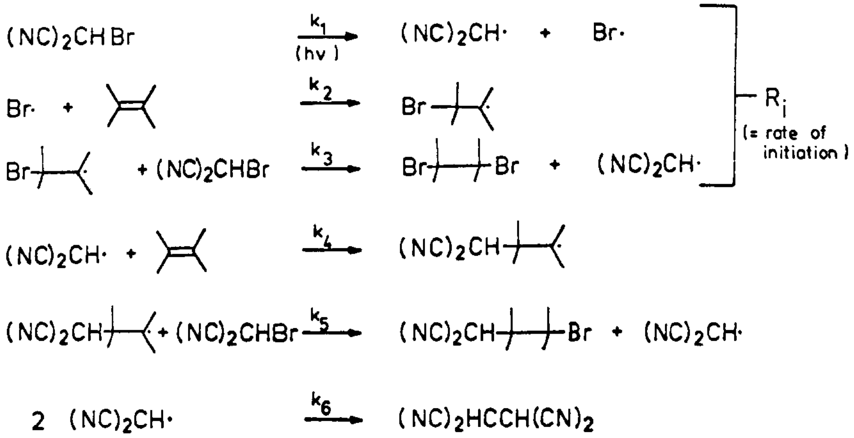
Bromomalononitrile adds to alkenes in a fast exothermic radical chain reaction (see scheme below) 2,3). The addition is well examined with respect to preparative aspects 2), stereochemistry 3) and regioselectivity 1). In order to get more informations about the relationship between reactivity and properties of the reactants we measured relative rate constants of dicyanomethyl radical additions to some simple alkenes. We hope that our results and their rationalisation 4,5) will shed some light on the controversial discussion about factors governing reactivity and regioselectivity in free radical addition.

Scheme



Our intentions were at first to determine the absolute rate constants of the addition step, k_4. The integrated equation of the pseudo first order reaction is 6):

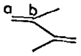
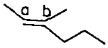
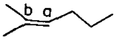
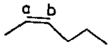
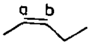
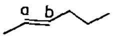
$$-\frac{\Delta \ln [\text{alkene}]}{\Delta t} = k_4\left(\frac{R_i}{2k_6}\right)^{0.5}$$

k_6 is known 7). We tried to determine the rate of initiation (R_i) using the inhibitor method 8). But the inhibitors (e.g. 2,6-di-tert. butyl-4-methylphenol, 1,4-benzoquinone) acted in some cases as initiators 4,9). There is a direct correlation of R_i with the lifetime (τ) of the radical chain 10), $R_i = (2k_6 \cdot \tau^2)^{-1}$. So we measured τ using the rotating sector method 10). Unfortunately the attainable accuracy was unsatisfactory with respect to the small differences in reactivity of the alkenes, we used (see table)11).However as we were able to show, R_i is constant in all additions we examined, when $[BrCH(CN)_2] : [\text{alkene}] \geqslant 10:1$ 12). So we measured relative rate constants k_{rel} 13).

The starting materials were purified by sublimation (bromomalononitrile) or destillation (alkenes, internal standards and solvent 1,2-dichloroethane). To remove oxygen the apparatous was flushed with nitrogen for 3 h. The irradiation (HBO 500/2 W mercury high pressure lamp, Bosch, West Germany) was performed in a thermostated Duran glass cell with quartz windows at 28.1 °C. During the whole reaction the transmission of the UV-light (365/366 nm) was greater than 82 % and practically constant (with the ratio $[BrCH(CN)_2] : [\text{alkene}] \geqslant 10:1$). The decrease of alkene concentration was measured by gaschromatography using n-heptane, n-octane or cyclohexane as internal standards (column: 20 % carbowax 20 M, chromosorb P). The pseudo first order kinetics was proved until an extent of reaction of more than 75 %. The half life periods were between 317 sec (addition to 2-methyl-1-pentene) and 5825 sec (addition to (E)-2-hexene). The rate constant for the addition to 2,3-dimethyl-1,3-butadiene was measured relative to that of the addition to 2-methyl-1-pentene under diminuation (to ca. 8.5 %) of the UV-light intensity used in all other cases. Under normal conditions its half life period was ca. 21 sec, i.e. the addition was then too fast for measuring 14). The irreversibility of addition was proved in the case of (Z)-2-pentene and (Z)-2-hexene 1) and should be probable in all others here regarded.

The results of our investigations are listed in the following table.

Table: Relative rate constants and regioselectivities 15) for the addition of dicyanomethyl radicals to various alkenes

alkene	k_{rel}	% addition	
		to C_a	to C_b
	273.1	⩾ 95	⩽ 5
	18.4	⩾ 95	⩽ 5
	15.0	⩾ 95	⩽ 5
	13.9	⩾ 95	⩽ 5
	1.16	⩾ 95	⩽ 5
	1.25	ca. 50	ca. 50
	1.23	ca. 50	ca. 50
	1.00	ca. 50	ca. 50

As we could show, all additions give nearly completely 1:1-adducts, other products not being detectable 1,4,16).

To rationalise the measured reactivities (k_{rel}) and the observed regioselectivities (see table) for the addition of dicyanomethyl radicals to alkenes by PMO-theory we calculated Fukui's superdelocalizability $S_r^{(R)}$ 17) for each addition and obtained a good linear correlation 4,5).

References and footnotes

++ Dedicated to Prof. Dr. Dr. e. h. H. Brockmann on the occasion of his 75th birthday.

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7 R. A. Kaba and K. U. Ingold, J. Am. Chem. Soc. 98, 523 (1976), $k_6 = 1.2\cdot10^9$ l$\cdot$mol$^{-1}\cdot$sec^{-1} (20 °C). Our measurements were performed at 28.1 °C. But the temperature coefficient for k_6 should be small with respect to the low activation energies of radical dimerisations.

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11 For the addition of dicyanomethyl radicals to 2-methyl-1-pentene we found: $\tau = (4.5 \pm 1.1)\cdot10^{-2}$ sec; $k_4 = (1.6 \pm 0.5)\cdot10^{6}$ l$\cdot$mol$^{-1}\cdot$sec^{-1} at 28.1 °C 4).

12 This was proved by measuring $k_4\cdot(R_i/2k_6)^{0.5}$ for the addition with the relative unreactive 1-pentene without and in presence of various amounts of the much more reactive 2-methyl-1-pentene, no change in rate of addition being detectable 4).

13 $k_{rel} = \left(k_4\cdot(R_i/2k_6)^{0.5}\right)_{\text{alkene}} : \left(k_4(R_i/2k_6)^{0.5}\right)_{\text{(E)-2-hexene}}$

14 For more experimental details and all data given in this work see ref. 4. The irradiation apparatous was constructed by H. Luthe (Dissertation, Universität Göttingen, West Germany, 1971) and W. Michaelis (Dissertation, Universität Göttingen, West Germany, 1971).

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