On the Reaction Mechanism of Scavenged Hydrocarbon Radiolysis

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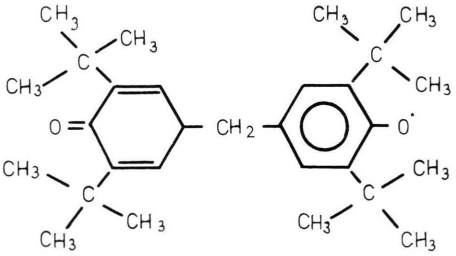
Dedicated to Professor G. O. Schenck on the occasion of his 70th anniversary

It is shown that in radiolysis not only the reaction of alkyl radicals with iodine, but also that of alkyl radicals with galvinoxyl is diffusion controlled. The activation energies of the reactions of alkyl radicals with iodine increase with molecular mass, following the Smoluchowski equation. In the gross reaction other reaction steps (*e.g.* polymerisation, combination) cover up this phenomenon.

It was found that in electron pulse radiolysis the rate constant of the cyclohexyl radical-iodine reaction is $1.2 \times 10^{10}\,M^{-1}\,s^{-1}$ at room temperature while that of the reaction of the radical with galvinoxyl (Go) amounts to only $8 \times 10^{8}\,M^{-1}\,s^{-1}$. The rate constants of analogous systems are close to these values [1, 2].



On the basis of the high rate constant of the cyclohexyl-iodine system it seemed to be proved that this alkyl radical-scavenger reaction is diffusion controlled but the question remained if this is also the case with the alkane-Go mixture. With this in mind we first measured the apparent activation energies of hydrocarbon-iodine and/or Go systems.

Gäumann, Rappoport and Ruf measured the E_A-values of dehydrogenation, C–C-scission, disproportionation, combination, dimerisation, polymerisation etc. of the C_5–C_{16} *n*-alkanes [3, 4]. From the *G*-values determined by gas chromatography after γ-irradiation with dose rates from 800 to 4200 μGy s^{-1} between -70 and $+25$ °C it was found that the E_A-values were between 0.8 and 3.0 kJ mol^{-1} although, due to ionic reactions, below -25 °C the activation energy was about -6 kJ mol^{-1}, *i.e.* it turned into the negative.

First we carried out experiments with a 5–1200 μGy s^{-1} dose rate ^{60}Co γ-irradiation and used spectrophotometrical evaluation. For the experimental details see [1] and [5]. The measured apparent activation energies are summarized in Table 1. The E_A data, also for the cyclopentane-iodine-Go ternary system, fall into the interval 0.9–2.5 kJ mol^{-1}. In view of the standard deviation of about ± 0.8 kJ mol^{-1} we did not succeed in reaching any conclusion as to the reaction mechanism or the molecular mass of the hydrocarbons or the scavengers. So we must agree with Gäumann's and others doubt: "Does such a unified treatment … make any sense?", and that the notion of apparent activation energy is, probably, an "oversimplification" [3].

Therefore we decided to determine by electron pulse radiolysis the rate constants of the reactions of

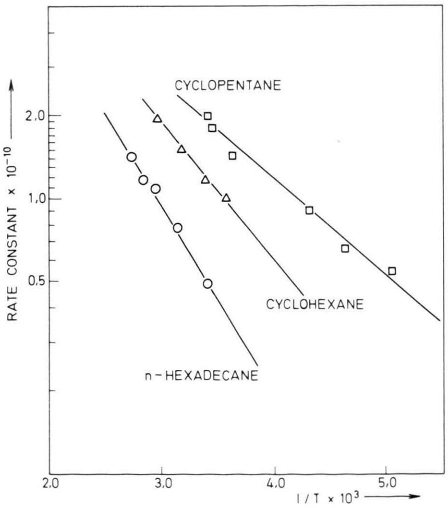


Fig. 1. Plots for activation energy determination of $R^{\bullet} + I_2$ reactions got by electron pulse radiolysis.

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Table 1. Apparent activation energies obtained by ^{60}Co γ-irradiation.

System		Dose rate	Temperature interval	Apparent activation energy
Compound	Scavenger conc. μM	mGy s^{-1}	°C	kJ mol^{-1}
Cyclopentane-	500 – 600	1100	− 80 ... + 25	2.5
-iodine	800 – 1000	1170	− 80 ... + 25	1.7
Cyclopentane-Go	15 – 20	5.5	− 80 ... + 25	0.9
n-Heptadecane-Go	15 – 20	5.5	− 30 ... + 110	2.5
Cyclopentane-				
-iodine-	200 – 250	280	− 80 ... + 25	1.1
-Go	15 – 20			

cyclopentane, cyclohexane, *n*-hexadecane with iodine, and that cyclopentane with Go between − 80 and + 110 °C. The most important advantage of these experiments is that they do not give apparent values of an unknown gross process but the rate constants and E_A-values of a known one: the $R^{\bullet}$ + scavenger reaction taking place in the mixtures.

According to Fig. 1, in the series of alkanes containing iodine the value of E_A increases with viscosity, in complete accordance with the Smoluchowski equation [1, 5], *i.e.* from 6.6 kJ mol^{-1} observed with cyclopentane through 9.1 kJ mol^{-1} with cyclohexane, to 12.9 kJ mol^{-1} with *n*-hexadecane.

The E_A-values got by pulse radiolysis of cyclopentane with iodine and Go are practically the same, 6.6 and 7.5 ± 10% kJ mol^{-1}, respectively. So it seems highly probably that the radical reactions not only with iodine but also with galvinoxyl are diffusion controlled, although in the latter case the chemical reaction is far slower.

The complex nature of the processes in pulse radiolysis of the ternary cycloalkane-iodine-galvinoxyl system was discussed in detail earlier [5].

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