Evidence for the Non-equilibration of Vibrational Excitation Energy in a Neopentane Molecule, Recently Labelled by Recoil Tritium

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Summary The reaction of hot recoil tritium atoms with neopentane can generate excited neopentane molecules which decompose by breaking the C–C bond nearest the labelling site; the excess energy is therefore not equilibrated before decomposition, $\tau_{\frac{1}{2}}$ (neopentane–^{3}H)* *ca.* 120 ps.

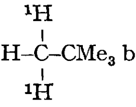
RECOIL tritium atoms [^{3}He (n,p) ^{3}H] can react with hydrocarbons by hydrogen replacement in a fast localised reaction.[1] Some of the labelled molecules that are produced contain enough vibrational excitation energy to subsequently undergo unimolecular decomposition, usually by C–C bond fission, less frequently by breaking C–H bonds.[2] Neopentane was chosen for this study to determine if the excess energy was completely equilibrated throughout the various vibrational modes of the molecule before decomposition. The radicals produced by bond rupture were detected as bromides. Widely different neopentane:bromine ratios were used. Detection was by gas-liquid chromatography and proportional counting,[3] the whole system being heated to 90° to enhance the vapour pressures of possible products such as t-butyl and neopentyl bromides. The fractions of the recoil tritium atoms available for reaction in the gas phase found in various products (P_i for product i) are summarised in the Table.

The yield of labelled t-butyl bromide was in all cases very low, usually below the limits of detection (max. P value, 0·002) whereas labelled methyl bromide was always observed

TABLE

Sample composition[a]			Yields of labelled products	
neopentane cmHg	bromine cmHg	neopentane : bromine ratio	P(neopentane-^{3}H)	P(methyl bromide-^{3}H)
8·30	20·60	0·40	0·125	0·017
8·82	11·39	0·77	0·141	0·020
8·92	8·92	1·00	0·154	0·015
5·36	5·36	1·00	0·205	0·022
60·08	40·03	1·50	0·174	0·015
26·11	13·08	2·00	0·153	0·019
28·96	11·98	2·42	0·148	0·014
50·81	20·15	2·52	0·163	0·014
10·27	3·14	3·27	0·146	0·018
27·29	7·99	3·42	0·156	0·017
22·28	5·72	3·90	0·156	0·018
61·89	15·38	4·02	0·159	0·012
57·88	11·40	5·07	0·173	0·013
25·93	4·93	5·26	0·159	0·016
67·20	9·98	6·73	0·172	0·016

[a] Quartz ampoules about 15—20 cm^3 also contained *ca.* 2 cmHg ^{3}He and received an integrated neutron flux of about 10^{15} cm^{-2} at 90°.

in a yield of about 10% neopentane-^{3}H. This demonstrates that the C–C bond that is broken is the one which is adjacent to the carbon where labelling has just taken place. The four C–C bonds are not equivalent throughout the molecule before decomposition. There is usually a significant yield of neopentyl bromide-^{3}H (P values, 0·006 ± 0·004) indicating that C–H bonds are also broken. If many electron volts of vibrational energy are more or less localised for tens or hundreds of pico-seconds in the  $^3\mathrm{H}\text{–}\overset{^1\mathrm{H}}{\underset{^1\mathrm{H}}{\mathrm{C}}}\text{–CMe}_3$ bonds then this is a very reasonable result even though D(C–H) > D(C–C).

Such energy localisation suggests that the vibrationally excited neopentane should have a short half-life; in fact a very slight pressure effect upon the yield of labelled methyl bromide can be detected. The ratio P(neopentane-^{3}H) : P (methyl bromide-^{3}H) rises linearly from 7 to 12 as the pressure of neopentane increases from 0 to 60 cmHg. This ratio is virtually independent of the original neopentane : bromine ratio, indicating that bromine plays no part in the formation of labelled radicals from (neopentane-^{3}H)*. Using the method of ref. 2 it can be shown that only 12% of the labelled neopentane molecules have sufficient excitation energy to decompose, and for those molecules with vibrational energy in excess of 3·5 eV [D(C–C), neopentane = 3·5 eV) their half-life is *ca.* 120 ps.

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