Tritium Exchange Reactions on Irradiated Silica Gel. Part I. Activation of Molecular Tritium and Application to the Tritium Labelling of Aliphatic Hydrocarbons

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The radiation-induced colour in silica gel is bleached when tritium gas is admitted and this bleaching process activates the tritium in such a way that when a hydrocarbon is later admitted it becomes labelled. Best yields (up to 130 mCi g^{-1}) are obtained for aliphatic hydrocarbons having a methyl group attached to a tertiary carbon atom, often with a high degree of radiochemical purity. The number of tritium atoms incorporated appears to be comparable with the number of F centres in the irradiated silica gel.

IT is known that various gases bleach the colour induced by γ-irradiation in silica gel,[1] often with simultaneous decomposition of the gas.[2,3] Kohn[4] has found that γ-irradiated silica gel promotes the exchange of hydrogen with deuterium, the radiation increasing the activity of the silica gel catalyst by a 'billion-fold.' We report here that we have found a similar effect in using irradiated silica gel to promote the exchange of tritium gas with aliphatic hydrocarbons. This method of labelling provides a useful alternative to the metal-catalysed[5,6] exchange reactions commonly used in labelling organic compounds.

EXPERIMENTAL

Samples (2 g) of silica gel (B.D.H. Laboratory Grade Reagent, 20—120 mesh) were degassed in a flask at 500 °C for 8 h using a rotary oil pump and mercury diffusion pump to a final pressure of 10^{-5} Torr. The degassed silica gel was then shaken into the Pyrex reaction ampoule shown

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[1] H. W. Kohn, *Nature*, 1959, **184**, 630.

[2] J. G. Rabe, B. Rabe, and A. O. Allen, *J. Phys. Chem.*, 1966, **70** (4), 1098.

[3] E. H. Taylor, *J. Chem. Educ.*, 1959, **36** (8), 396.

[4] H. W. Kohn and E. H. Taylor, *J. Phys. Chem.*, 1959, **63**, 966.

[5] M. A. Long and A. L. Odell, *J. Chem. Soc.* (*A*), 1969, 2475, and earlier papers.

[6] J. L. Garnett, *Nucleonics*, 1962, **20** (12), 86.

in the Figure and sealed off under vacuum. (If the solid was not thoroughly degassed in this manner, it was not coloured by the radiation and did not promote the exchange reaction.)

The irradiations were carried out in a 100 Ci cobalt-60 source for 15 h, a dose of some 1·0 Mrad being received by the sample. Because the radiation-induced colour of the silica gel is extremely air sensitive the reactants were admitted under vacuum as follows: constriction A was broken off, under vacuum (10^{-5} Torr) in a stopcock (while the ampoule was held by an 0-ring seal in a ground-glass socket). Tritium gas (30 mCi) was then admitted while the solid (in the lower bulb of the ampoule) was immersed in liquid nitrogen. Constriction B was then sealed off and the solid allowed to warm to room temperature when the colour was bleached, by the tritium, within a few minutes. The tritium was left on the silica gel for a period which we call the ' tritium activation time ' until needed in a labelling reaction, when constriction C was broken, under vacuum, and the hydrocarbon (0·1 ml) vapour-transferred onto the solid using liquid nitrogen. The apparatus was then re-evacuated, before constriction D was sealed off, to remove any traces of vapour which might otherwise pyrolyse on the hot glass. Both reactants were left on the solid for 1 h before reaction products were removed by heating the silica gel to 160 °C and cold-trapping them in the side-arm. The side-arm was then broken off and a sample of hydrocarbon injected, with a syringe, into a gas chromatograph equipped with a flame-ionisation detector and also an ion chamber for detecting tritium radiation.

TABLE 1

Activity yields (in μCi) from reaction of isopentane (0·1 ml) and tritium gas (30 mCi) on γ-irradiated silica gel. Tritium activation time 1 h at 18 °C

		Product yields (μCi)				
Amount of SiO_2 (wt/g)	% of Total T_2 present incorporated (%)	Ethane	Propane	Isobutane	Isopentane (% radiochemical purity)	2,2-Dimethylbutane
2	27	27 ± 3	15 ± 4	170 ± 40	7 800 ± 300 (97%)	10 ± 4
5	55	5	5	650	15 300 (96%)	36

In degradative chlorination experiments the labelled isopentane (50 μl) was heated with chlorine gas (1 ml) at 300 °C for 1 h. Reaction products were again analysed in the gas chromatograph.

E.s.r. measurements to determine the concentration of F-centres were performed at room temperature on gas-free irradiated silica gel using a Varian V-4502 spectrometer.

RESULTS

Isopentane.—When isopentane was admitted to the tritium–silica gel system it became labelled as shown in Table 1. The only byproduct detected by the flame-ionisation detector was isobutane which showed up as an extremely small peak, all other byproducts being ' weightless.'

TABLE 2

Effect of tritium activation time on yield of labelled isopentane

Irradiated silica gel		Unirradiated silica gel	
Tritium activation time/h	Yield (μCi)	Tritium activation time/h	Yield (μCi)
10	9 550	5	0
15	9 080	50	7·5
20	10 200	200	31·7
50	9 950		
200	9 800		
500	9 830		

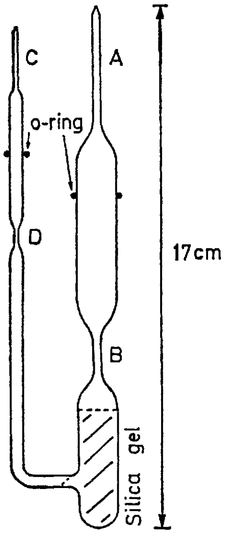
In control experiments with unirradiated silica gel no detectable labelling was found for short tritium activation times and only slight yields for longer times (Table 2).

The total amount of tritium incorporated was independent of the amount of isopentane used if above 10 μl.

TABLE 3

Effect of changing total amount of tritium on the amount of tritium incorporated into isopentane (0·1 ml) by irradiated silica gel (2 g)

Amount of tritium used (mCi)	Amount of tritium incorporated (mCi)	(atoms)
3	0·6	$1{\cdot}2 \times 10^{16}$
10	3	6×10^{16}
22	5	1×10^{17}
30	9	$1{\cdot}8 \times 10^{17}$
60	10	2×10^{17}
90	10	2×10^{17}
110	10	2×10^{17}



The reaction ampoule used in the tritium labelling of hydrocarbons on irradiated silica gel

Increasing the reaction time of the isopentane with the tritium on the silica gel above 10 min, and increasing the amount of tritium used above 30 mCi (0·5 μmol) (Table 3), produced no increase in the amount of tritium incorporated. If isopentane was admitted to the irradiated silica gel and allowed to bleach the colour before the tritium was admitted, no detectable labelling occurred. When the tritium and the isopentane were admitted together the yields of labelled products were only slightly lower than those obtained when the tritium was admitted first.

TABLE 4

Percentage activities of degradation products produced by chlorination of labelled isopentane

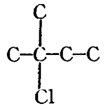
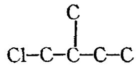
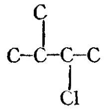
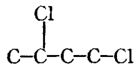
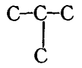
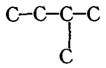
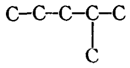
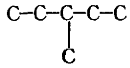
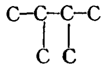
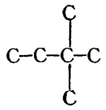
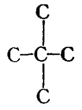
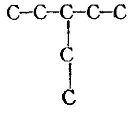
Product	Distribution of mass (%)	Distribution of activity (%)
 $\mathrm{C{-}\overset{C}{\underset{Cl}{C}}{-}C{-}C}$	30	30
 $\mathrm{Cl{-}C{-}\overset{C}{C}{-}C{-}C}$	24	25
 $\mathrm{C{-}\overset{C}{C}{-}\underset{Cl}{C}{-}C}$	16	15
 $\mathrm{C{-}\overset{Cl}{C}{-}C{-}C{-}Cl}$	30	30

TABLE 5

Variation of yield of labelled hydrocarbon with structure of the hydrocarbon

Conditions: 2 g irradiated silica gel, 0·1 ml hydrocarbon, 30 mCi tritium, 1 h tritium activation time at 18 °C

Structure	Yield of labelled hydrocarbon (μCi)	Radiochemical purity (%)
C–C–C–C–C–C	75	70·7
C–C–C–C–C	242	80·3
C–C–C–C	1 700	96·3
 $\mathrm{C{-}\underset{C}{C}{-}C}$	6 260	98·3
 $\mathrm{C{-}C{-}\underset{C}{C}{-}C}$	7 140	98·0
 $\mathrm{C{-}C{-}C{-}\underset{C}{C}{-}C}$	4 090	95·3
 $\mathrm{C{-}C{-}\underset{C}{C}{-}C{-}C}$	4 125	94·0
 $\mathrm{C{-}\underset{C}{C}{-}\underset{C}{C}{-}C}$	8 600	96·1
 $\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}C}$	125	36·0
 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C}$	527	40·1
 $\mathrm{C{-}C{-}\underset{\underset{C}{C}}{C}{-}C{-}C}$	600	13·1

The tritium activation time has been increased up to 500 h without sensibly changing the yield of labelled products (Table 2). The reactivity of the sorbed tritium was destroyed, however, by heating the tritium/silica gel system above 200 °C for 1 h.

In degradative experiments the labelled isopentane was allowed to react with chlorine gas to produce all four possible monohalides and the specific activities of the four products were found to be identical (Table 4).

Other Hydrocarbons.—Other aliphatic hydrocarbons have been studied and results are shown in Table 5.

F-Centres in Alkali Halides.—In a previous publication [7] we reported that n-pentane can be labelled with tritium on γ-irradiated silica gel and on γ-irradiated alkali halides. We have since confirmed the work on silica gel but have found the results reported on alkali halides to be due to pyrolysis by hot glass during sealing-off operations and not to the action of the colour centres.

DISCUSSION

The bleaching of the radiation-induced colour in silica gel by the tritium activates the tritium in such a way that it can exchange with hydrocarbons. The process by which the tritium bleaches the colour must be thermally activated because the colour does not fade at liquid-nitrogen temperatures. The persistence of this activated form of tritium may be due to the trapping of the activated tritium (possibly atomic tritium) in micro-slits or crystal lattice vacancies on the silica gel in the same way as the hydrogen atoms produced by the radiolysis of the hydroxy-groups are stabilised.[8]

An indication of how rapidly the activation process occurs can be inferred from the result that the amount of tritium incorporated is only very slightly lower when both reactants are admitted together than when the tritium is activated first, the tritium gas apparently being activated before the isopentane vaporises enough to bleach the colour. The isopentane must also react fairly rapidly with the activated tritium because the 10 min reaction time is approximately the time required for the frozen isopentane to vaporise.

The maximum amount of tritium incorporated into the isopentane under these reaction conditions (Table 3) is *ca.* 2×10^{17} atoms which corresponds roughly to the number of F-centres found in the irradiated silica gel by e.s.r. spin counting (*ca.* $1{\cdot}5 \times 10^{17}$ centres per 2 g of SiO_2), suggesting a possible 1 : 1 relationship between the two. F-Centres in silica gel are stable at temperatures of up to 200 °C (ref. 9) and we have found that if the tritium–silica gel system is heated above this temperature the tritium loses its reactivity also indicating some significant relationships between the F-centres and the activated tritium.

Our results obtained with the other hydrocarbons indicate the branched-chain hydrocarbons are more heavily labelled than straight-chain hydrocarbons. The chain length appears to be important, as does the presence of a tertiary carbon atom, in producing a high yield of labelled hydrocarbon. That the hydrogen atom attached to the tertiary carbon atom is not preferentially

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[7] B. J. Cowell, K. M. Matthews, and A. L. Odell, *Chem. Comm.*, 1971, 1264.

[8] V. B. Kazansky, G. B. Pariisky, and V. V. Voevodsky, *Discuss. Faraday Soc.*, 1961, **31**, 203.

[9] C. M. Nelson and J. H. Crawford, *J. Phys. Chem. Solids*, 1960, **13**, 296.

exchanged, however, is established by the degradation experiment using chlorine, in which the 2-chloro-2-methylbutane does not have a lower specific activity than the other halide products (Table 4).

The presence of a tertiary carbon atom alone, however, is not sufficient to ensure a high activity yield which appears to require a tertiary C-methyl group (see the case of 3-ethylpentane in Table 5).

The nature of the activated tritium, the mechanism by which it reacts with the hydrocarbons and the reasons for the structural effects remain uncertain at this stage. Investigation of these matters is continuing.

In spite of the above uncertainties, it is clear that good yields of labelled aliphatic hydrocarbons can be obtained often with a high standard of radiochemical purity indicating that this labelling method may well prove to be of general application as a synthetic procedure. Studies on the labelling of other types of compounds are in hand.

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