496. *Beta Energy Recoil Effects of Carbon-14 in Toluene and Ethylbenzene.*

By P. G. Manning and C. B. Monk.

Recoil energy from carbon-14 beta particles in [*Me*-^{14}C]toluene is found to cause negligible bond rupture, as judged by the yield of aniline, while with [α-^{14}C]ethylbenzene about 15—20% bond rupture occurs. This is in line with a concept of rupture being caused by electronic excitation.

The recoil energy arising from the β-emission of carbon-14 in gaseous ethane was found by Wolfgang, Anderson, and Dodson [1] to cause about 53% bond rupture, as shown by the yield of methylamine. Quantum-mechanical calculations by Wolfsberg [2] indicate that, through rotational and vibrational excitation, the extent of rupture should be about 40%. Although such calculations are approximate, some of the difference between the two mentioned figures can be attributed to electronic excitation of the daughter product being localised in the C–N bond, and this results in additional breakdown.[3] It has been suggested by Wolfgang [3] that studies of the present two examples should help to show if this view has any foundation, for the benzene ring should promote delocalisation of any electronic excitation, this being more marked with aniline than with benzylamine. In addition, improved analyses have been attempted [1] by using tritiated materials, since the amount of amine produced or left after carbon-14 decay, after separation from the parent hydrocarbon, can be assessed from its tritium count-rate and that of its parent (allowing for carbon-14).

The recoil kinetic energy, E_{R}, associated with β^- emission is given by [4]

$$E_{\mathrm{R}} = E_\beta(M_\beta + M_0)/2M_{\mathrm{R}} \qquad (1)$$

where M_{R} is the mass of the recoil atom, E_β is the energy of the β^- particle, M_β and M_0 are the relativistic and rest masses of a β^- particle, respectively. Also, with c = velocity of light,

$$E_\beta = (M_\beta - M_0)c^2, \qquad (2)$$

so that

$$E_{\mathrm{R}} = E_\beta^{\,2}/2c^2M_{\mathrm{R}} + E_\beta M_0/M_{\mathrm{R}} \qquad (3)$$

and, with M_0 and M_{R} in mass units,

$$E_{\mathrm{R}} = E_\beta^{\,2}/1862M_{\mathrm{R}} + E_\beta M_0/1848M_{\mathrm{R}}. \qquad (4)$$

If E_{B} is the bond energy, the component of kinetic energy (E_{D}) is the most important factor with regard to bond rupture, and $E_{\mathrm{D}} = E_{\mathrm{R}}m/(m + M)$ where m is the mass of the recoiling atom and $(m + M)$ is that of the molecule. Also, according to the approximate calculations by Wolfsberg,[2] for ethane, about 60% of E_{R} appears as rotational and vibrational energy, so that, for bond-breaking, $E_{\mathrm{B}} < 0{\cdot}6E_{\mathrm{D}}$. Since E_β(max.) is 0·155 Mev, from eqn. (4), E_{R}(max.) = 6·9 ev, whence, for toluene, $E_{\mathrm{D}} = 6{\cdot}9 \times 0{\cdot}6 \times 14/93 = 0{\cdot}6$ ev, and for ethylbenzene, $E_{\mathrm{D}} = 0{\cdot}55$ ev. So, since [5] $E_{\mathrm{D}} = 2{\cdot}1$ ev for C–N and 4 ev for C–H bond rupture should not occur in the present compounds as the result of the β^- recoil energy. As the data and calculations below show, this is so for toluene but not for ethylbenzene for which there is about 15—20% bond rupture. This is about the same as for ethane and appears to confirm the interpretations of Wolfgang [1,3] and Wolfsberg,[2] *i.e.*, bond rupture results from electronic excitation. Such an effect would be rapidly delocalised by the benzene ring of aniline but impeded by the intervening methylene group in benzylamine.

[1] Wolfgang, Anderson, and Dodson, *J. Chem. Phys.*, 1956, **24**, 16.
[2] Wolfsberg, *J. Chem. Phys.*, 1956, **24**, 24.
[3] Wolfgang, private communication.
[4] Davies, *J. Phys. Chem.*, 1948, **52**, 595.
[5] Pauling, "The Nature of the Chemical Bond," 3rd edn., Cornell University Press, 1960.

EXPERIMENTAL

Dibromobenzene was treated with tritiated water (Radiochemical Centre) to form tritiated benzene[6] whose monobromo-derivative was subjected to a Wurtz–Fittig reaction[7] with [^{14}C]methyl iodide (Radiochemical Centre). About 2 ml. of purified doubly-labelled toluene (DLT) were obtained. A sample of untritiated [α-^{14}C]toluene (LT) was also made.

Benzyl bromide and [^{14}C]methyl iodide were treated by the Wurtz–Fittig method; the product was brominated and then tritiated to form tritiated [α-^{14}C]ethylbenzene (DLEB). An untritiated form (LEB) was also made. Inactive ethylbenzene, aniline, and benzylamine were fractionally distilled. Thiophen-free toluene was prepared by Vogel's method.[7]

Pyrex-glass bulbs with narrow necks and vacuum stopcocks were used for the decay studies. After evacuation, open glass ampoules with weighed amounts of DLT or DLEB cooled by solid carbon dioxide were placed in the necks which were then sealed. After the stopcocks were opened, the bulbs were stored for 7—8 months in vacuum desiccators at 10 mm. pressure, cooled, and opened, about 100 mg. of the relevant hydrocarbon and amine were added, and the whole was extracted with ether. Samples were separated by gas chromatography (Perkin-Elmer unit) at 125°. Toluene was collected after 5 min. and aniline after 40 min. For ethylbenzene and benzylamine the times were 20 min. and 50 min. Other samples were separated by extracting the amines with dilute hydrochloric acid and washing this with toluene–ether; the amines were acetylated and assayed for tritium.

The tritium and carbon-14 count-rates were obtained by liquid scintillation methods (Nuclear Enterprises equipment). Solutions for counting were 5 ml. of scintillator [0·3% of DPO (2,5-diphenyloxazole), 0·01% of POPOP (1,4-bis-5′-phenyloxazol-2′-yl)benzene in toluene], 2 ml. of alcohol, 0·2 g. of water, and 0·2 g. of sample. At least 15,000 counts were recorded and corrected for background (about 100 c.p.m.).

RESULTS AND CALCULATIONS

Toluene–Aniline System.—The count-rate due to carbon-14 in the doubly-labelled toluene (DLT) samples was found by using the same sample of [^{14}C]methyl iodide to form the untritiated labelled toluene (LT). For the latter, 1·247 g. of [^{14}C]methyl iodide were diluted to 10·31 g. with inactive methyl iodide, and 211 mg. of this solution were likewise diluted to 40·14 g. before reaction with excess of bromobenzene. The dilution factor was thus 1572. Also, by comparison with a sodium [^{14}C]carbonate reference (Radiochemical Centre), the counting efficiency was established as 22·4%, so if one curie is taken as 3·700 × 10^{10} c.p.s., the carbon-14 content of the LT and hence that of the DLT sample was found.

Dil. LT (mg.)	c.p.m. (^{14}C)	c.p.m./g. of LT	Activity/min.-g.	^{14}C/g. of LT
213·7	8826	41,300	1·828 × 10^5	129·4 μc
202·4	8362	41,310	1·828 × 10^5	129·4 μc

The tritium count-rate of the DLT sample was obtained after dilution of 904 mg. to 216·7 g. (250 ml.) with inactive toluene and dilution of 938 mg. of this likewise. The dilution factor is thus 5·54 × 10^6.

Run	Dil. DLT (mg.)	c.p.m. (^{3}H)	c.p.m. (^{3}H)/g. of DLT
1	206·3	314,450	8·44 × 10^{10}
2, 3,	201·5	322,670	8·86 × 10^{10}

It is easily ascertained that the carbon-14 contribution to these count-rates is negligible.

Now, the DLT as made contained only a tiny fraction that was labelled with both tritium and carbon-14. By calling this pure DLT, its proportion was calculated by use of

$$W = -(\mathrm{d}N/\mathrm{d}t)t_{\frac{1}{2}}M/2\cdot303 \times 6\cdot023 \times 10^{23} \log 2, \qquad (5)$$

where W is the weight of isotope of mass M, absolute decay-rate $-\mathrm{d}N/\mathrm{d}t$ and half-life $t_{\frac{1}{2}}$. Since the carbon-14 content of the DLT was equal to that of the LT sample, $-\mathrm{d}N/\mathrm{d}t =$ 129·4 μc/g. while $t_{\frac{1}{2}} = 5570$ yr., the proportion of pure DLT in the DLT is 0·01895%.

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[6] Wilson and Weldon, *J.*, 1946, 235.

[7] Vogel, " Textbook of Practical Organic Chemistry," 3rd edn., Longmans, Green, London, 1956.

The amounts (in terms of tritium count-rates) of pure tritium-labelled aniline (TLA) produced were estimated from the count-rates of the aniline carrier containing its labelled form and the value just derived.

Run	DLT (mg.)	Aniline + TLA (mg.)	Counted (mg.)	c.p.m. (^{3}H)	c.p.m. (^{3}H)/g. of pure TLA
1	90·1	281·0	205·7	95·0	$7{\cdot}60 \times 10^6$
2	92·6	238·7	209·3	116·9	$7{\cdot}60 \times 10^6$
3	276·6	244·5	208·8	359·1	$8{\cdot}02 \times 10^6$

Theoretical amounts of DLT changed into TLA were calculated with the aid of the expression

$$\ln(N/N_0) = -t(\ln 2)/t_{\frac{1}{2}} \tag{6}$$

this being used to obtain the ratio N/N_0, N_0 being the initial c.p.m. and N that of carbon-14 after time t. Now $N/N_0 = N'/N_0'$ = (residual DLT)/(residual DLT + pure TLA formed) and N_0' = c.p.m. (^{3}H) g. of DLT as given in the second set of calculations. Thus, $N_0' - N'$ = c.p.m. (^{3}H)/g. of pure TLA, if no bond fission occurred, can be calculated. As the following figures show, the calculated amounts of LTA formed agree closely with those of the last column above, *i.e.*, the amount of bond fission is negligible.

Run	t (yr.)	N_0/N	N_0'	$N_0' - N'$	% (C–N) bond fission
1	0·726	1·0000903	$8{\cdot}44 \times 10^{10}$	$7{\cdot}62 \times 10^6$	0
2	0·714	1·0000888	$8{\cdot}86 \times 10^{10}$	$7{\cdot}87 \times 10^6$	3·5
3	0·739	1·0000920	$8{\cdot}86 \times 10^{10}$	$8{\cdot}15 \times 10^6$	1·5

Ethylbenzene–Benzylamine System.—1·076 g. of [^{14}C]methyl iodide was diluted to 15·176 g. with the inactive form and 3·063 g. of this was diluted to 34·274 g. before forming [α-^{14}C]ethylbenzene, giving a dilution factor of 157·8. Comparison with the sodium [^{14}C]carbonate reference showed the counting efficiency to be 20·4%.

Dil. LEB (mg.)	c.p.m. (^{14}C)	c.p.m./g. of LEB	Activity/min.-g.	^{14}C/g. of LEB
207·7	55,590	267,650	$1{\cdot}312 \times 10^6$	93·25 μc
205·3	54,745	266,660	$1{\cdot}307 \times 10^6$	92·90 μc

For the tritium count-rate of the DLEB, 1017 mg. were diluted to 216·2 g. with inactive ethylbenzene and 1268 mg. of this were similarly diluted, so the dilution factor is $3{\cdot}626 \times 10^4$.

Run	Dil. DLEB (mg.)	c.p.m. (^{3}H)	c.p.m. (^{3}H)/g. of DLEB
1	203·4	402,440	$7{\cdot}17 \times 10^{10}$
2	206·1	410,460	$7{\cdot}22 \times 10^{10}$

By use of eqn. (5) as before, $W = 2{\cdot}032 \times 10^{-5}$ g. of ^{14}C/g. of DLEB, the corresponding weight of DLEB $= 1{\cdot}567 \times 10^{-4}$ g., so 0·01567% of the DLEB is labelled with both isotopes, *i.e.*, this is the pure DLEB. The amounts of tritium-labelled benzylamine (TLB) formed were estimated from portions of the carrier containing TLB.

Run	DLEB (mg.)	Benzylamine + TLB (mg.)	Counted (mg.)	c.p.m. (^{3}H)	c.p.m. (^{3}H)/g. of pure TLB
1	106·4	223·6	201·5	88·4	$5{\cdot}29 \times 10^6$
2	207·8	223·7	202·5	179·6	$5{\cdot}52 \times 10^6$

The ratio N/N_0 was calculated from eqn. (6), and N_0' and N' calculated as before.

Run	t (yr.)	N_0/N	N_0'	$N_0' - N'$	% (C–N) bond fission
1	0·739	1·0000920	$7{\cdot}17 \times 10^{10}$	$6{\cdot}60 \times 10^6$	20
2	0·739	1·0000920	$7{\cdot}22 \times 10^{10}$	$6{\cdot}64 \times 10^6$	17

The evidence thus obtained supports the suggestion that the benzene can delocalise electronic excitations produced by carbon-14 decay; with aniline this effect is sufficient to eliminate bond rupture while the intervening methylene group in benzylamine retards the energy transference sufficiently for some of it to break down some C–N bonds. Such conclusions depend on the assumption that isotopic exchange of tritium does not occur; examples of evidence to support this are that, in solution, the rate of hydrogen exchange is dependent on the acidity of the medium,[8] while, in the gas phase, high-energy tritium atoms are needed to effect exchange with organic molecules.[9]

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THE EDWARD DAVIES CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

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[8] Gold and Long, *J. Amer. Chem. Soc.*, 1953, **75**, 4543.

[9] Kee, Musgrove, and Rowland, *J. Amer. Chem. Soc.*, 1959, **81**, 3802; Wolf, *Ann. Rev. Nuclear Sci.*, 1960, **10**, 259.