595. *Properties and Reactions of Free Alkyl Radicals in Solution. Part IV.* The Direct Reaction between Alkyl Radicals and Aliphatic Aldehydes.*

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The free radical $\cdot CMe_2\cdot CO_2Me$ attacks saturated aliphatic aldehydes at 80—110° to a slight extent only. Decarbonylation of the resulting $R\cdot CO\cdot$ radicals then follows as a short chain reaction :

$$R\cdot CO\cdot \longrightarrow R\cdot + CO;\ R\cdot + R\cdot CHO \longrightarrow RH + R\cdot CO\cdot$$

and small amounts of the corresponding paraffin hydrocarbons are formed. There is some indication that chain ending leads to the production of the keto-esters $R\cdot CO\cdot CMe_2\cdot CO_2Me$. Carbon tetrachloride effectively stops the decarbonylation chain by reacting with the $R\cdot CO\cdot$ radicals to form acyl chlorides.

In the vapour phase it has been established conclusively (Steacie, " Atomic and Free Radical Reactions," 1946, Reinhold Publ. Corp., N.Y., pp. 120—132, 178—200) that both the thermal and the photochemical decomposition of aldehydes are predominantly radical-chain processes :

$$X\cdot + R\cdot CHO \longrightarrow XH + R\cdot CO\cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$R\cdot CO\cdot \longrightarrow R\cdot + CO \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$R\cdot + R\cdot CHO \longrightarrow RH + R\cdot CO\cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which the chain-initiating radical $X\cdot$ may be either the radical $R\cdot$ resulting from a primary decomposition, $R\cdot CHO \longrightarrow R\cdot + \cdot CHO$, or atomic hydrogen produced by the breakdown of the unstable $\cdot CHO$ radical (cf. equation 2). Even under favourable

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conditions the chain lengths for the decarbonylations of the lower aliphatic aldehydes are short and it has been concluded that both processes (2) and (3) require an appreciable activation energy.

Hitherto this reaction has been little studied in the liquid phase. In a brief note Winstein and Seubold (*J. Amer. Chem. Soc.*, 1947, **69**, 2916) have reported 90% decarbonylation of β-phenyl*iso*valeraldehyde in 5 hours at 130°, when methyl radicals derived from the thermal decomposition of di-*tert.*-butyl peroxide are used as initiators, but they observed scarcely any reaction at 80° when using benzoyl peroxide as their catalyst. Kharasch, Urry, and Kuderna (*J. Org. Chem.*, 1949, **14**, 248) found that the decarbonylation of *n*-heptanal occurs at as low a temperature as 65° as a side reaction in the acetyl peroxide-catalysed addition of this aldehyde to olefins, and was evident even at 0° in conjunction with the photochemical addition of acetaldehyde to oct-1-ene. At this low temperature it was at first doubted whether *free* R·CO· radicals are formed (Bamford and Norrish, *J.*, 1938, 1531), but the successful addition of acetaldehyde to oct-1-ene under these conditions must be regarded as conclusive evidence. From this experiment Kharasch, Urry, and Kuderna also isolated a little diacetyl, and concluded therefore that the chain-ending reaction was probably (4) :

$$2R{\cdot}CO{\cdot} \longrightarrow R{\cdot}CO{\cdot}CO{\cdot}R \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

They also noted that only the saturated aliphatic aldehydes lost carbon monoxide.

Since 2-carbomethoxy-2-propyl radicals, $\cdot CMe_2{\cdot}CO_2Me$, can conveniently be made by the thermal decomposition of dimethyl αα′-azo*iso*butyrate in homogeneous solution in the temperature range of 80—110°, and both the natures and the relative percentages of their self-interaction products have been studied accurately (Bickel and Waters, *Rec. Trav. chim.*, 1950, **69**, 312), we have used these radicals, as X· in equation (1), to initiate the liquid-phase decarbonylation of aliphatic aldehydes. In all cases the extent of reaction (1) between the $\cdot CMe_2{\cdot}CO_2Me$ radicals and the aldehyde was so slight that clear evidence of it could only be obtained by using high concentrations of the azo-ester and volumes of material sufficiently large to permit careful fractional distillations of the eventual reaction products. Table 1 summarises the results obtained by heating solutions of the azo-ester in aldehydes for about an hour at 80—110° so that a slow, controllable reaction occurred.

TABLE 1. *The decomposition of dimethyl αα′-azo*iso*butyrate in aliphatic aldehydes.*

		n-Heptanal	*n*-Octanal	*n*-Decanal	3 : 5 : 5-Trimethylhexanal	2-Ethylhexanal
Quantity of aldehyde	g.	34·5	38·5	46·9	35·6	48·5
	mol.	0·30	0·30	0·30	0·25	0·38
Quantity of azo-ester......	g.	11·35	11·25	11·6	15·6	14·2
	mol.	0·049	0·05	0·05	0·068	0·062
	mol. fraction	0·16	0·17	0·17	0·27	0·16
Carbon monoxide evolved	c.c.	700	445	—	750	—
	g.	0·9	0·5	0·95	0·9	0·95
as % of aldehyde		11	6	11	13	9
as % of $\cdot CMe_2{\cdot}CO_2Me$ radicals		31	20	32	25	29
Hydrocarbon (RH) isolated		*n*-Hexane	*n*-Heptane	*n*-Nonane	2 : 4 : 4-Trimethylpentane	*n*-Heptane
	g.	1·1	0·9	1·8	2·3	1·5
Methyl *iso*butyrate isolated	g.	1·47	1·3	1·8	2·75	2·7
as % of $\cdot CMe_2{\cdot}CO_2Me$ radicals *		15	13	18	22	21

* In an inert solvent 15% of methyl *iso*butyrate is formed (Bickel and Waters, *loc. cit.*).

From each reaction the total loss of gaseous products was 60—70% more than that corresponding to the theoretical loss of nitrogen from the azo-ester, and analysis established that carbon monoxide had been liberated. The fractions of lowest boiling point were in each case the paraffins, RH, corresponding to the aldehydes R·CHO. These paraffins were characterised carefully by elementary analysis and physical constants, so as to confirm that at the temperature used there did not occur any degradation of the alkyl radicals,

$C_6H_{13}\cdot$, etc., to olefins by the disproportionation reactions which are known to occur in the higher-temperature gas reactions.

The small amount of methyl *iso*butyrate formed in aldehyde solutions shows that most of the carbon monoxide formation must be due to a chain reaction in which the aldehyde molecules R·CHO are attacked by alkyl radicals R·.

Careful searches were made amongst the higher-boiling fractions of the various reaction mixtures for substances diagnostic of particular chain endings. Possibilities are (*a*) higher paraffins, R·R; (*b*) high-boiling ketones or 1 : 2-diketones, R·CO·R, R·CO·CO·R; (*c*) esters, $R\cdot CMe_2\cdot CO_2Me$; (*d*) ketonic esters, $R\cdot CO\cdot CMe_2\cdot CO_2Me$. The isolation of products, however, is an extremely difficult task since the attack on the aldehyde is so slight, and consequently there always preponderate reaction products such as $MeO_2C\cdot CMe_2\cdot CMe_2\cdot CO_2Me$, $MeO_2C\cdot CMe_2\cdot CH_2\cdot CHMe\cdot CO_2Me$, and $MeO_2C\cdot CMe_2\cdot CH_2\cdot CMe(CO_2Me)\cdot CMe_2\cdot CO_2Me$ which arise from the dimerisation and disproportionation of the $\cdot CMe_2\cdot CO_2Me$ radicals (Bickel and Waters, *loc. cit.*). There is moreover the serious difficulty that the *n*-aldehydes easily undergo self-condensation and subsequent dehydration (to substances of crotonaldehyde type) when heated, giving high-boiling products which readily interact with all reagents that can be used for the characterisation of ketones. Nevertheless some indication of the occurrence of reaction (5), viz.:

$$R\cdot CO + \cdot CMe_2\cdot CO_2Me \longrightarrow R\cdot CO\cdot CMe_2\cdot CO_2Me \quad . \quad . \quad . \quad . \quad (5)$$

has been obtained with heptanal, since on hydrolysis the high-boiling residues yielded a little *iso*butyric acid which was characterised as its *S*-benzylthiuronium salt. Compounds of type (*c*) may be present though this is not certain, and there was no evidence for the occurrence of reaction (4). Chain ending by (5) is to be expected under our experimental conditions, since it involves the two radicals of least reactivity in the whole system.

Winstein and Seubold (*loc. cit.*) also reported that with both β-phenyl*iso*valeraldehyde and *iso*valeraldehyde the reaction chain (2, 3) was inhibited when carbon tetrachloride was added to the decomposing mixture, owing to the intervention of reactions (6) and (7):

$$R\cdot CO\cdot + CCl_4 \longrightarrow R\cdot COCl + \cdot CCl_3 \cdot \quad . \quad . \quad . \quad . \quad . \quad (6)$$
$$R\cdot CHO + \cdot CCl_3 \longrightarrow R\cdot CO\cdot + CHCl_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

We have found that this reaction is general. As Table 2 shows, very little carbon monoxide indeed is evolved from decompositions of dimethyl αα'-azo*iso*butyrate in dry aldehyde–carbon tetrachloride mixtures under nitrogen. The products of these reactions were fractionated and the portions of both lower and higher boiling point were then treated with water. Significant amounts of ionisable chlorine were found to be associated with the fractions of boiling point 130° or over, so that acyl chlorides are undoubtedly formed. When air was not excluded, some carbonyl chloride was formed: this is indicative of the presence of $\cdot CCl_3$ radicals, and did not occur in the absence of the aldehydes (cf. Part III). Attempts to isolate the small amounts (1—2 g.) of the acyl chlorides failed because of the closeness of their boiling points to those of the corresponding aldehydes. Though the expected carboxylic acids were formed by hydrolysis it may be argued that these could have arisen by autoxidation of the aldehyde during the necessary manipulations.

TABLE 2. *Decompositions of dimethyl αα'-azo*iso*butyrate in aldehyde–carbon tetrachloride mixtures.*

Each mixture contained 0·1 mole of aldehyde, 0·2 mole of carbon tetrachloride, and 0·016 mole (3·85 g.) of the azo-ester.

Aldehyde	Total gas evolved, c.c. (N.T.P.)	CO, c.c.	Acyl chloride (by titration)	
			mol. $\times 10^{-3}$ (=% of R·CHO)	as % of $\cdot CMe_2\cdot CO_2Me$ radicals
None	375	—	—	—
Benzaldehyde	372	—	3	9
n-Heptanal	370	—	12	36
n-Octanal	385	10	6	19
n-Decanal	390	15	9·5	31
3 : 5 : 5-Trimethylhexanal	396	21	17	54
2-Ethylhexanal	454	79	14	43

This series of experiments showed that some reaction does occur between $\cdot CMe_2\cdot CO_2Me$ radicals and benzaldehyde to give benzoyl radicals and thence benzoyl chloride, though the direct reaction between $\cdot CMe_2\cdot CO_2Me$ radicals and carbon tetrachloride is insignificant. Thus, as Kharasch, Urry, and Kuderna (*loc. cit.*) have concluded, the absence of carbon monoxide formation from benzaldehyde is due to the resonance stability of the benzoyl radical, and not to any great difference in the ease of homolysis of the C–H bonds of aromatic and aliphatic aldehydes.

Tables 1 and 2 indicate that there are significant differences in reactivity between the *n*-aldehydes and their branched-chain analogues, but since, during the heating, the *n*-aldehydes may be undergoing the concurrent reaction, $2R\cdot CH_2\cdot CHO \longrightarrow R\cdot CH_2\cdot CH{=}CR\cdot CHO + H_2O$, we do not think that it is justifiable to suggest possible relations between chemical structure and reactivity.

EXPERIMENTAL

*Decomposition of Dimethyl αα'-Azo*iso*butyrate.*—(1) *In* n-*heptanal.* The azo-ester (11·35 g., 0·049 mole), dissolved under nitrogen in *n*-heptanal (34·6 g., 0·303 mole) in a flask connected through a reflux condenser and a cold trap to a large gas burette, was heated gently to about 90° so that gas evolution occurred steadily at as low a temperature as possible. After 1½ hours, when reaction had ceased, the total gas evolution amounted to 1800 c.c. (corr. to N.T.P.). This corresponded almost exactly to the observed loss of weight (2·23 g.) of total products. Examination in a mass spectrometer showed that this gas consisted almost entirely of nitrogen and carbon monoxide, and that hydrogen and simple gaseous hydrocarbons were absent.* The liquid products were fractionated under dry nitrogen, giving (i) 4·1 g., b. p. 60—110°/750 mm., (ii) 25·2 g., b. p. 140—152°/750 mm., (iii) 3·9 g., b. p. 50—95°/11 mm., and (iv) 6·1 g., b. p. 99—165°/11 mm. Fraction (i) was refluxed for 2 hours with methanolic potassium hydroxide. The solution was then distilled, from a steam-bath, and the distillate was diluted with water. Two layers separated. The upper of these was washed with water, dried (KOH), and distilled. It gave 1·1 g. of *n*-hexane, b. p. 68·5°, n_D^{16} 1·3782 (corr. to n_D^{20} 1·3761), d_{16}^{16} 0·668 (Found : C, 83·7; H, 16·6. Calc. for C_6H_{14} : C, 83·7; H, 16·3%). *n*-Hexane has b. p. 69·0°, n_D^{20} 1·3754, d_{16}^{20} 0·661.

The residue from this hydrolysis was dissolved in water, aldehydic condensation products were removed by extraction with ether, and after acidification the aqueous solution was again extracted with ether. It yielded 1·27 g. of *iso*butyric acid (equiv. to 1·47 g. of methyl *iso*butyrate) which was identified by conversion into its *S*-benzylthiuronium salt, m. p. 144°.

Fractions (ii) and (iii) consisted of unchanged heptanal. Fraction (iv) gave an orange-red 2 : 4-*dinitrophenylhydrazone*, m. p. 129·5°, which had an absorption maximum at 3850 Å (Found : C, 61·4; H, 7·4; N, 14·5. $C_{20}H_{30}O_4N_4$ requires C, 61·5; H, 7·7; N, 14·4%). By direct comparison this was shown to be identical with the 2 : 4-dinitrophenylhydrazone of the self-condensation and dehydration product of *n*-heptanal, *i.e.*, $C_6H_{13}\cdot CH{=}C(C_5H_{11})\cdot CHO$ which, it was then found, is formed when *n*-heptanal is refluxed for an hour under nitrogen.

Fraction (iv) was refractionated under nitrogen, giving (*a*) 2·4 g., b. p. 120—130°/11 mm., and (*b*) 1·65 g., b. p. 150—152°/12 mm. Portion (*a*) was refluxed for 4 hours with methanolic potassium hydroxide. The solvent and unsaponified products were removed and the aqueous residue was acidified and distilled in steam. Volatile acids (0·9 g.) were collected in ether and, after removal of the ether, were kept at 0° for some days, whereupon part (0·6 g.) solidified. The liquid remainder smelt of *iso*butyric acid and yielded its *S*-benzylthiuronium salt of m. p. and mixed m. p. 144°. The solid acid, after crystallisation from light petroleum, proved to be tetramethylsuccinic acid. A further 0·6 g. of this substance was also isolated from the residue from the steam-distillation. Alkaline hydrolysis of (*b*) also yielded a trace of *iso*butyric acid.

(2) *In* n-*octanal.* Decomposition of the azo-ester (1·25 g.) in *n*-octanal (38·5 g.) was carried out similarly and gave 1543 c.c. of gas (N.T.P.), the loss of weight being 1·9 g. On distillation there were obtained (i) 4·1 g., b. p. 80—100°/752 mm., (ii) 25·5 g., b. p. 163—168°/752 mm., (iii) 3·1 g., b. p. 60—90°/9 mm., and (iv) 13 g., b. p. 90—200°/9 mm. Fraction (i) was dissolved in ether, extracted with aqueous sodium hydrogen sulphite to remove aldehydes, and then refluxed with methanolic potassium hydroxide for 2 hours. By following the procedure given above there was obtained 0·9 g. of *n*-heptane, b. p. 96°, n_D^{19} 1·3893, d_{17}^{17} 0·682 (Found : C, 83·7;

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H, 16·1. Calc. for C_7H_{16} : C, 84·0; H, 16·0%). *n*-Heptane has b. p. 98·4°, n_D^{20} 1·3876, d_{20}^{20} 0·684. The alkaline residue after acidification gave 1·15 g. of *iso*butyric acid, b. p. 150°, corresponding to 1·3 g. of methyl ester. Fractions (ii) and (iii) consisted of *n*-octanal, whilst (iv) contained 2-*n*-hexyldec-2-enal, which gave an orange-red 2 : 4-*dinitrophenylhydrazone* of m. p. and mixed m. p. 100° (Found : C, 63·9; H, 8·3; N, 13·1. $C_{22}H_{34}O_4N_4$ requires C, 63·2; H, 8·1; N, 13·4%). Only 0·1 g. of volatile acid, b. p. 140—150°, was isolated by alkaline hydrolysis of this fraction, besides 1·9 g. of tetramethylsuccinic acid.

(3) *In* n-*decanal.* The decomposition of the azo-ester (11·6 g.) in *n*-decanal (46·9 g.) gave 2·37 g. of gaseous products. There were isolated (i) 2·4 g., b. p. 60—65°/120 mm., (ii) 43·7 g., b. p. 65—95°/11 mm., (iii) 3·8 g., b. p. 95—175°/11 mm., and (iv) 3·6 g., b. p. 175—190°/11 mm. Fraction (i) after alkaline hydrolysis yielded *iso*butyric acid, b. p. 150°, equivalent to 1·8 g. of methyl ester. Fraction (ii) gave 2·8 g., b. p. 55—80°/11 mm., which after treatment with bisulphite, etc., eventually yielded 1·8 g. of *n*-nonane, b. p. 148—150°, n_D^{35} 1·3980 (corr. to n_D^{20} 1·4055), d_{22}^{22} 0·7158 (Found : C, 83·3; H, 15·1. Calc. for C_9H_{20} : C, 84·4; H, 15·6%). *n*-Nonane has b. p. 150·8°, n_D^{20} 1·4055, d_{20}^{20} 0·7177.

The higher-boiling portion of fraction (ii), and fraction (iii), comprised unchanged aldehyde, whilst (iv) contained 2-*n*-octyldodec-2-enal, from which was prepared a 2 : 4-*dinitrophenylhydrazone*, m. p. 84° (Found : C, 65·6; H, 8·6; N, 11·7. $C_{26}H_{42}O_4N_4$ requires C, 65·6; H, 8·9; N, 11·8%).

(4) *In 2-ethylhexanal.* The decomposition of the azo-ester (14·2 g.) in 2-ethylhexanal (48·5 g.) gave 2·7 g. of gaseous products. Fractionation of the liquid gave (i) 7·6 g., b. p. 65—115°/760 mm., (ii) 36·3 g., b. p. 120—160°/760 mm., (iii) 2·1 g., b. p. 40—70°/10 mm., and (iv) 7·9 g., b. p. 95—153°/8 mm. After removal of aldehyde and subsequent alkaline hydrolysis fraction (i) gave 1·8 g. of *n*-heptane, b. p. 97°, n_D^{14} 1·3910 (corr. to n_D^{20} 1·3880), d_{18}^{18} 0·687 (Found : C, 83·7; H, 16·1%). From the alkaline hydrolysis residue there were obtained 2·3 g. of *iso*butyric acid, corresponding to 2·7 g. of the methyl ester. Fractions (ii) and (iii) consisted of unchanged aldehyde, whilst (iv) contained dimethyl tetramethylsuccinate and similar products. Alkaline hydrolysis of the fractions of high boiling point yielded only a trace of *iso*butyric acid.

(5) *In* 3 : 5 : 5-*trimethylhexanal.* The decomposition of the azo-ester (15·6 g.) in 3 : 5 : 5-trimethylhexanal gave 2270 c.c. of gas (at N.T.P.); the loss of weight as gaseous products was 2·9 g. Distillation yielded (i) 5·4 g., b. p. 60—95°/759 mm., (ii) 29·0 g., b. p. 135—160°/759 mm., (iii) 6·8 g., b. p. 95—140°/12 mm., and (iv) 4·5 g., b. p. 155—195°/12 mm. Fraction (i), after alkaline hydrolysis for 4 hours, gave 2·3 g. of 2 : 4 : 4-trimethylpentane, b. p. 98—99°, $n_D^{15\cdot5}$ 1·3948, d_{18}^{18} 0·694 (Found : C, 84·5; H, 15·4. Calc. for C_8H_{18} : C, 84·2; H, 15·8%). 2 : 4 : 4-Trimethylpentane has b. p. 99·2°, n_D^{20} 1·3914, d_{20}^{20} 0·692; an authentic specimen was found to have $n_D^{15\cdot5}$ 1·3949. From the alkali there were separated 2·4 g. of *iso*butyric acid, b. p. 150°, corresponding to 2·75 g. of methyl ester. Fraction (ii) consisted of unchanged aldehyde, whilst (iii) and (iv) contained dimethyl tetramethylsuccinate and similar products. The non-volatile residue yielded a trace of *iso*butyric acid after alkaline hydrolysis. No unsaturated aldehyde was formed under these conditions.

Decompositions in the Presence of Carbon Tetrachloride.—The decompositions of dimethyl αα'-azo*iso*butyrate in aldehyde–carbon tetrachloride mixtures, summarised in Table 2, were carried out under similar conditions : in each case 3·85 g. (0·0167 mole) of the azo-ester, 0·10 mole of the aldehyde, and 0·20 mole of carbon tetrachloride were used. The following reaction with *n*-heptanal is typical.

The mixture was heated gently till gas evolution set in, and it was finally refluxed for 4 hours to ensure complete reaction. Air had previously been displaced from the apparatus by dry nitrogen. The gas evolved was equivalent to 370 c.c. at N.T.P., whilst the calculated volume of nitrogen liberated from the azo-ester is 375 c.c. The liquid products were fractionally distilled in dry nitrogen. The carbon tetrachloride portion was acid, and washing with water gave a solution containing, by Volhard titration, 0·012 g. of chloride anion.

The fraction of higher boiling point was washed with 2N-ammonia; this aqueous layer was then made up to a standard volume and its chloride content was determined by Volhard titrations of aliquot parts. There had been liberated 0·012 mole of chloride anions, equivalent to formation of 1·73 g. of *n*-heptanoyl chloride. Characterisation both as amide and as anilide was attempted, but in each case the condensation of the free aldehyde with the base vitiated success.

When these decompositions were carried out in air, acrid fumes were evolved both during the decomposition of the azo-ester and during the distillation of the carbon tetrachloride later. By reaction of the vapours with aniline it was shown that carbonyl chloride was present in appreciable amount. This was not noticeable when the azo-ester was boiled in carbon tetrachloride in the absence of an aldehyde.

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