253. *The Isomerism of the Oximes. Part XLIII. The Kinetics of the Pyrolysis of Acyl Derivatives.*

By Douglas Ambrose and O. L. Brady.

A kinetic study has been made of the pyrolysis of acyl derivatives of the aldoximes: $\mathrm{X{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OR = X{\cdot}C_6H_4{\cdot}CN + HOR}$.

The reaction shows first-order kinetics, and the rate constants are in the order X = *o*-MeO > *p*-$\mathrm{Me_2N}$ > *p*-MeO > 3 : 4-$\mathrm{CH_2O_2}$ > H > *m*-MeO > *o*-$\mathrm{NO_2}$ > *m*-$\mathrm{NO_2}$ = *p*-$\mathrm{NO_2}$; R = $\mathrm{Cl_3C{\cdot}CO} \gg \mathrm{Ph_2N{\cdot}CO} > \mathrm{EtO{\cdot}CO} >$ *p*-$\mathrm{NO_2{\cdot}C_6H_4{\cdot}CO} > \mathrm{PhCO} >$ *p*-$\mathrm{MeO{\cdot}C_6H_4{\cdot}CO} = \mathrm{CH_2Cl{\cdot}CO} > \mathrm{Ac}$.

The mechanism of the reaction is discussed and it is suggested that the pyrolysis can best be represented as involving electron shifts, without separation of charges, in a structure of the acyl compound in which hydrogen bonding is present.

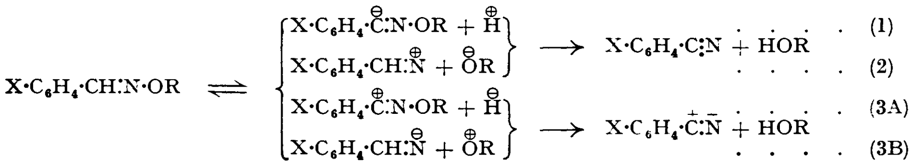
The formation of nitriles by the pyrolysis of acyl derivatives of aldoximes has been known for some time; for example, Neber, Hartung, and Ruopp (*Ber.*, 1925, **58**, 1239) found that benzoyl-α-*p*-nitrobenzaldoxime, heated for 30 minutes at 140°, gave benzoic acid and a quantitative yield of *p*-nitrobenzonitrile, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OBz \longrightarrow BzOH + NO_2{\cdot}C_6H_4{\cdot}CN}$, and similar results were obtained with other acyl derivatives by Lindemann and Thiele (*Annalen*, 1926, **449**, 74), von Auwers and Krese (*ibid.*, **450**, 283), and Lindemann, Könitzer, and Romanoff (*ibid.*, 1927, **456**, 284). In addition, one of us has observed that the carefully purified acetyl derivatives of some substituted α-benzaldoximes, prepared in the course of other investigations, when kept in tightly corked tubes in the dark for several years, decomposed and acquired an odour of acetic acid and nitrile. This was noticed in the case of the acetyl derivatives of α-*p*-methoxy-, α-3 : 4-dimethoxy-, and α-3 : 4-methylenedioxy-benzaldoximes, but the acetyl derivatives of α-*m*- and α-*p*-nitrobenzaldoximes under similar conditions remained practically unchanged. This suggested that the electron-demand or -release of the substituted benzene nucleus had considerable influence on the rate of decomposition.

A kinetic study has now been made of this pyrolysis at various temperatures in xylene and in the absence of solvents.

The reaction shows first-order kinetics, and the general result of varying the substituent X in the nucleus in compounds of the general formula $\mathrm{X{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OR}$ indicates a decrease in the rate constant in the order *o*-MeO > *p*-$\mathrm{Me_2N}$ > *p*-MeO > 3 : 4-$\mathrm{CH_2O_2}$ > H > *m*-MeO > *o*-$\mathrm{NO_2}$ > *m*-$\mathrm{NO_2}$ = *p*-$\mathrm{NO_2}$ (Tables I—IV).

Variations in R produce a decrease in rate constant in the order $\mathrm{Cl_3C{\cdot}CO}$ * $\gg \mathrm{Ph_2N{\cdot}CO} > \mathrm{EtO{\cdot}CO} >$ *p*-$\mathrm{NO_2{\cdot}C_6H_4{\cdot}CO} > \mathrm{Bz} >$ *p*-$\mathrm{MeO{\cdot}C_6H_4{\cdot}CO} = \mathrm{CH_2Cl{\cdot}CO} > \mathrm{Ac}$ (Table V).

The possible mechanisms of the decomposition may be represented:



$$\mathrm{X{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OR} \rightleftharpoons \left\{\begin{array}{l} \left.\begin{array}{l} \mathrm{X{\cdot}C_6H_4{\cdot}\overset{\ominus}{C}{:}N{\cdot}OR} + \overset{\oplus}{\mathrm{H}} \\ \mathrm{X{\cdot}C_6H_4{\cdot}CH{:}\overset{\oplus}{N}} + \overset{\ominus}{\mathrm{O}}\mathrm{R} \end{array}\right\} \longrightarrow \mathrm{X{\cdot}C_6H_4{\cdot}C{\vdots}N + HOR} \quad \begin{array}{r} \dots\dots\ (1) \\ \dots\dots\ (2) \end{array} \\ \left.\begin{array}{l} \mathrm{X{\cdot}C_6H_4{\cdot}\overset{\oplus}{C}{:}N{\cdot}OR} + \overset{\ominus}{\mathrm{H}} \\ \mathrm{X{\cdot}C_6H_4{\cdot}CH{:}\overset{\ominus}{N}} + \overset{\oplus}{\mathrm{O}}\mathrm{R} \end{array}\right\} \longrightarrow \mathrm{X{\cdot}C_6H_4{\cdot}\overset{+}{C}{:}\overset{-}{N} + HOR} \quad \begin{array}{r} \dots\dots\ (3A) \\ \dots\dots\ (3B) \end{array} \end{array}\right.$$

$$\begin{array}{rcl} \mathrm{X{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OR} & \rightleftharpoons & \mathrm{X{\cdot}C_6H_4{\cdot}\dot{C}{:}N{\cdot}OR} + \dot{\mathrm{H}} \\ \mathrm{X{\cdot}C_6H_4{\cdot}\dot{C}{:}N{\cdot}OR} & \longrightarrow & \mathrm{X{\cdot}C_6H_4{\cdot}C{\vdots}N} + \dot{\mathrm{O}}\mathrm{R} \\ \dot{\mathrm{H}} + \dot{\mathrm{O}}\mathrm{R} & \longrightarrow & \mathrm{HOR} \quad \dots\dots\dots\dots \quad (4A) \end{array}$$

$$\begin{array}{rcl} \mathrm{X{\cdot}C_6H_4{\cdot}CH{:}NOR} & \rightleftharpoons & \mathrm{X{\cdot}C_6H_4{\cdot}CH{:}\dot{N}} + \dot{\mathrm{O}}\mathrm{R} \\ \mathrm{X{\cdot}C_6H_4{\cdot}CH{:}\dot{N}} & \longrightarrow & \mathrm{X{\cdot}C_6H_4{\cdot}C{\vdots}N} + \dot{\mathrm{H}} \\ \dot{\mathrm{H}} + \dot{\mathrm{O}}\mathrm{R} & \longrightarrow & \mathrm{HOR} \quad \dots\dots\dots\dots \quad (4B) \end{array}$$

Mechanisms (1), (2), (3A), and (3B) represent heterolytic fissions, and (4A) and (4B) homolytic fissions. (4A) and (4B) might occur simultaneously, as suggested for the

---

* From qualitative observations only.

decomposition of the diazoacetates in non-ionising solvents (Grieve and Hey, *J.*, 1934, 1797) :

$$\mathrm{R{\cdot}N{:}N{\cdot}OAc} \longrightarrow \dot{\mathrm{R}} + \mathrm{N}\vdots\mathrm{N} + \dot{\mathrm{O}}\mathrm{Ac}$$

$$\mathrm{CHPh{:}N{\cdot}OAc} \longrightarrow \dot{\mathrm{H}} + \mathrm{Ph{\cdot}C}\vdots\mathrm{N} + \dot{\mathrm{O}}\mathrm{Ac} \quad \ldots\ldots \quad (4C)$$

or might give rise to chain reactions :

$$\mathrm{X{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OR} \longrightarrow \mathrm{X{\cdot}C_6H_4{\cdot}CH{:}}\dot{\mathrm{N}} + \dot{\mathrm{O}}\mathrm{R}$$

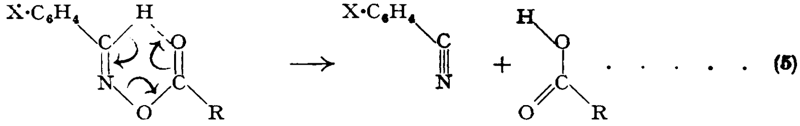
$$\mathrm{X{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OR} + \dot{\mathrm{O}}\mathrm{R} \longrightarrow \mathrm{X{\cdot}C_6H_4{\cdot}}\dot{\mathrm{C}}\mathrm{{:}N{\cdot}OR} + \mathrm{HOR}$$

$$\mathrm{X{\cdot}C_6H_4{\cdot}}\dot{\mathrm{C}}\mathrm{{:}N{\cdot}OR} \longrightarrow \mathrm{X{\cdot}C_6H_4{\cdot}C}\vdots\mathrm{N} + \dot{\mathrm{O}}\mathrm{R} \quad \ldots\ldots \quad (4D)$$

Mechanism (1) is ruled out because electron-recession due to X from the methine-carbon atom would favour the reaction, and electron-accession retard it, whereas the opposite is the case. Neither (3A) nor (3B) leading to the other canonical form of the nitrile would be favoured by increasing the electron-attracting nature of R and such fissions seem unlikely.

On the other hand, the observed effects of electronic displacements on the rate constants support mechanism (2), but there are objections to its adoption in so simple a form. First, it involves an ionisation with the consequent large energy barrier to be overcome; this might be accomplished if there was solvation of ions but this is not likely to occur to any extent in xylene; moreover, there was no marked increase in the rate of reaction in benzonitrile; further in the case of the carbethoxy-derivatives the rate constant was generally higher in the absence of solvent (Table IV). Secondly, the effects due to variation in X and R are small compared with those observed in the hydrolysis of substituted carboxylic esters; for example, the rate constant for the pyrolysis of carbethoxy-*p*-methoxybenzaldoxime is about 3·6 times greater than that of carbethoxy-*p*-nitrobenzaldoxime, and that of *p*-nitrobenzoyl-*p*-methoxybenzaldoxime only about 1·6 times greater than that of *p*-methoxybenzoyl-*p*-methoxybenzaldoxime, whereas that for the hydrolysis of ethyl *p*-nitrobenzoate is at least 500 times greater than that of ethyl *p*-methoxybenzoate (Ingold and Nathan, *J.*, 1936, 222; Evans, Gordon, and Watson, *J.*, 1937, 1430; 1938, 1439).

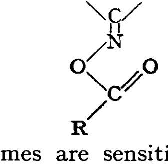
If, however, hydrogen bonding exists in the acyl derivatives of α-aldoximes as suggested by Benger and Brady (*J.*, 1950, 1221) the pyrolysis can be represented as involving electron shifts without separation of charges :



. . . . . . (5)

This mechanism is free from the objections to (2) indicated above; no ionisation is involved, electron-release from $\mathrm{X{\cdot}C_6H_4}$– would favour the rupture of the N–O bond but hinder the rupture of the C–H bond, and the effect of passing from X = *p*-MeO to X = *p*-$\mathrm{NO_2}$ would be less than in the hydrolysis of the ethyl benzoates since the pyrolysis is conditioned by two factors influenced in opposite senses by the substituent group. Electron-withdrawal by R, whilst it would retard the electron shift from the doubly-bound oxygen atom, would favour it from the nitrogen–oxygen bond which is probably the determining factor in the reaction. In this connection one may note the extreme instability of the trichloroacetyl derivatives, even trichloroacetyl-α-*p*-nitrobenzaldoxime decomposing when kept at room temperature for a few hours (Benger and Brady, *loc. cit.*).

Further information would be afforded on the validity of the hypothesis in reaction (5) by the study of the pyrolysis of acetyl-β-aldoximes where hydrogen bonding would not readily occur :



Unfortunately the acetyl-β-aldoximes are sensitive to traces of acids, being isomerised rapidly thereby to the α-compounds; so, since acetic acid is one of the products of the decomposition, they cannot be used. Possibly the carbethoxy-compounds would be free from this objection as the ethyl hydrogen carbonate first formed decomposes to carbon dioxide and ethanol: $R{\cdot}CH{:}NO{\cdot}CO_2Et \longrightarrow RCN + HO{\cdot}CO_2Et \longrightarrow CO_2 + HOEt$; but, so far, it has not been found possible to prepare carbethoxy-β-aldoximes.

A qualitative investigation has been made of the pyrolysis of carbanilino-α- and -β-aldoximes (Sharawy, unpublished), but the reaction is complicated by the phenylcarbamic acid first formed decomposing in two ways, to give aniline and diphenylurea, and it has not been possible yet to work out a reliable analytical technique for following the reaction kinetically:

$$\begin{aligned} R{\cdot}CH{:}NO{\cdot}CO{\cdot}NHPh &\longrightarrow RCN + HO{\cdot}CO{\cdot}NHPh \\ HO{\cdot}CO{\cdot}NHPh &\longrightarrow CO_2 + PhNH_2 \\ 2HO{\cdot}CO{\cdot}NHPh &\longrightarrow CO_2 + H_2O + CO(NHPh)_2 \end{aligned}$$

In addition carbanilino-β-benzaldoxime gave some benzaldehyde, indicating a different mode of decomposition.

Many pyrolyses are now regarded as taking place by homolytic fission, and mechanisms (4A), (B4), (4C), and (4D) cannot be excluded.

The effect of electron-accession or *vice versa* on the rate constant of homolytic fission reactions does not seem to be established. It has been suggested by Grieve and Hey (*loc. cit.*) and Waring and Abrams (*J. Amer. Chem. Soc.*, 1941, **63**, 2757) that the decomposition of the diazoacetates in non-ionising solvents involves homolytic fission. Now the rate constant for the decomposition of $X{\cdot}C_6H_4{\cdot}N{:}N{\cdot}OR$ is practically uninfluenced by the nature of X but is markedly influenced by the nature of R in the order $HCO < MeCO < EtCO < n\text{-}C_3H_7CO$ (Hey and Waters, *J.*, 1948, 882), but in the decomposition of compounds of the type $p\text{-}X{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}O{\cdot}CO{\cdot}C_6H_4Y\text{-}p$ the ratio $k(X = MeO)/k(X = NO_2)$ is as much as 3·5 : 1, whilst $k(Y = NO_2)/k(Y = MeO)$ is only 1·6 : 1.

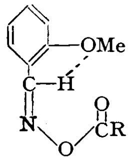
The absence of by-products in the reaction is rather against homolytic fission; the formation of the very sparingly soluble *p*-nitrobenzylideneazine, $NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2$, which might be formed by the pairing of $NO_2{\cdot}C_6H_4{\cdot}CH{:}N$ radicals in (4B) could not have escaped notice but small quantities of other by-products might have done so.

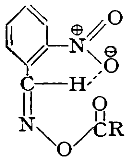
Copper has a pronounced catalytic effect on the decomposition (cf. Waters, *J.*, 1942, 266), and the effect of this and other catalysts is being further investigated. On the other hand mercury is not attacked during the pyrolysis, nor are copper salts formed in the presence of calcium carbonate as is observed when free acyl radicals are produced (Waters, *J.*, 1937, 113; Hey and Waters, *J.*, 1948, 882).

The rate constants bring out certain interesting points. It will be seen from Tables II and IV that *m*-MeO retards decomposition as compared with H, whilst *p*-MeO accelerates it; this is in the order of dissociation constants of the acids $X{\cdot}C_6H_4{\cdot}CO_2H$ where $m\text{-}MeO > H > p\text{-}MeO$.

Although the dissociation constant of the *o*-acid is little lower than that of *p*-methoxybenzoic acid the velocity of decomposition of *o*-methoxy-compounds is considerably greater than that of the corresponding *p*-methoxy-derivatives.

Tables I and II indicate that the rate constants for *o*-nitro-compounds are appreciably higher than for the corresponding *m*- and *p*-nitro-derivatives although the dissociation constant of *o*-nitrobenzoic acid is some 20 times that of *m*- or *p*-nitrobenzoic acid. These results suggested that the possibility of hydrogen bonding between the methine-hydrogen atom and an atom of the *o*-substituent favours the rupture of the C–H bond:





just as in the case of α-*o*-nitrobenzaldoxime it favours attack on the methine-hydrogen atom by $\overset{\ominus}{O}H$ (Benger and Brady, *loc. cit.*).

The *m*-nitro-compounds apparently decompose somewhat more slowly than the corresponding *p*-nitro-compounds, but it is doubtful if our results are sufficiently accurate to place these compounds in their correct order, and the ratio of the dissociation constants of the corresponding benzoic acids is only 1 : 1·17, so that further speculation on these results is uncalled for.

TABLE I.

Rates of pyrolysis of $X{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OAc$ *in xylene* ; k × 10^5 *sec.*$^{-1}$.

X.	139°.	120°.	115°.
m-NO_2	8·4	—	0·86
p-NO_2	9·2	—	—
o-NO_2	12·1	—	—
3 : 4-CH_2O_2	19·2	—	1·57
p-MeO	26·5	—	1·95
p-Me_2N	69	4·4	2·92

TABLE II.

Rates of pyrolysis of $X{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OBz$ *in xylene*; k × 10^5 *sec.*$^{-1}$.

X.	139°.	130°.	120°.	115°
m-NO_2	31·0	8·8	3·4	—
p-NO_2	—	8·8	—	—
o-NO_2	—	13·0	—	—
m-MeO	—	—	9·2	5·4
H	100	—	11·5	5·6
p-MeO	too fast to measure.	—	16·1	11·1
o-MeO		—	30·7	17·6

TABLE III.

Rates of pyrolysis of $X{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}O{\cdot}CO{\cdot}CH_2Cl$ *in xylene at* 139°.

X.	*m*-NO_2.	*p*-NO_2.	*o*-NO_2.	3 : 4-CH_2O_2.
k × 10^5, sec.$^{-1}$	27·0	32·5	32·5	92·0

TABLE IV.

Rates of pyrolysis of $X{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}O{\cdot}CO_2Et$ *at* 118·6°; *k* × 10^5 sec.$^{-1}$.

X.	In xylene.	Fused, no solvent.
m-NO_2	16·1	—
p-NO_2	17·0	17·7
o-NO_2	27·1	45·9
m-MeO	46·2	50·9
H	50·6	51·0
p-MeO	61·1	73·6
p-Me_2N	112	156
o-MeO	183	336

TABLE V.

Rates of pyrolysis of $X{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OY$; *k* × 10^5 sec.$^{-1}$.

	X = *p*-MeO.			X = *m*-NO_2.		X = H.
Y.	139°.	120°.	115°.	139°.	118·6°.	118·6°.
$Ph_2N{\cdot}CO$	—	—	—	—	36·7	106
EtO·CO	—	61·1 (118·6°)	—	—	16·1	—
p-$NO_2{\cdot}C_6H_4{\cdot}CO$	—	22·4	—	—	—	—
Bz	too fast	16·1	11·1	31·0	3·4 (120°)	—
p-MeO·$C_6H_4{\cdot}CO$	—	12·4	—	—	—	—
$CH_2Cl{\cdot}CO$	115	—	—	27·0	—	—
Ac	26·5	—	1·95	8·4	0·86 (115°)	—

EXPERIMENTAL.

Preparation of Materials.—The acyl derivatives of the aldoximes were prepared by known methods and recrystallised until the m. p.s corresponded to those in the literature or until a constant m. p. was obtained after 2 successive crystallisations. The thermometer was checked with a standard. A number of discrepancies were observed, *viz.* :

Chloroacetyl-α-*p*-nitrobenzaldoxime, m. p. 128°, chloracetyl-α-*p*-methoxybenzaldoxime, m. p. 72°; Benger and Brady (*loc. cit.*) found 131° and 60° respectively. Benzoyl-α-*m*-nitrobenzaldoxime, m. p. 175°; Brady and McHugh (*J.*, 1925, **127**, 2414) found 161°.

The carbethoxy-derivatives had m. p.s : *m*-NO_2 95° (97°), *p*-NO_2 108° (109°), *o*-NO_2 42° (42°) ; *o*-MeO 50°, (52°) ; H 36—37° (34—35°) ; *p*-MeO 73° (74°) ; *p*-Me_2N 116° (118°). The figures in parentheses are those given by Brady and Dunn (*J.*, 1916, **109**, 650), or Brady and McHugh (*J.*, 1923, **123**, 1190).

*Carbethoxy-α-*m*-methoxybenzaldoxime* crystallised from light petroleum in colourless needles, m. p. 43° (Found : C, 59·5; H, 5·5; N, 6·4. $C_{11}H_{13}O_3N$ requires C, 59·2; H, 5·8; N, 6·3%) ; *p*-methoxybenzoyl-α-*p*-methoxybenzaldoxime had m. p. 149° and *p*-nitrobenzoyl-α-*p*-methoxybenzaldoxime, m. p. 153° both crystallised from benzene.

Commercial xylene was dried over sodium and distilled, the middle 80% being collected.

Kinetic Measurements by Determination of Acid.—*Acetyl derivatives.* A weighed sample (1—2·5 g.) of the acetyl compound and 25 c.c. of xylene were placed in a round-bottomed flask with ground-glass joint and reflux condenser, and the mixture was rapidly heated to boiling. At suitable intervals the flask was cooled for 15 minutes to avoid loss of acetic acid when breaking the seal between flask and condenser, and a sample withdrawn by a pipette. No allowance was made for the periods of cooling and re-heating, but as far as possible the times of such operations were kept constant. This somewhat crude technique adopted in the earlier experiments was not refined, as the accuracy with which the acetic acid could be determined did not seem to justify it. The withdrawn sample was weighed, water added (15—20 c.c.), and the acid titrated with N/30-barium hydroxide using phenolphthalein. Considerable difficulty was experienced in observing the end point in the titration; unless water was added first, an emulsion of water in xylene was formed and no end point could be obtained; if too much water was added the end point became indistinct and transitory; attempts to extract the acid before titration did not improve the accuracy. As examples of the results four separate determinations with acetyl-α-*m*-nitrobenzaldoxime gave $k \times 10^5$ varying from 6·9 to 8·8 sec.$^{-1}$ (mean 8·4), with acetyl-α-3 : 4-methylenedioxybenzaldoxime 16·5—22·2 (mean 19·2) and with acetyl-α-*p*-methoxybenzaldoxime 23·0—28·4 (mean 26·5). Even if the extreme values were taken the order of the compounds was not altered.

Later experiments were carried out at 120° and 115° (thermostat) by the method described for the benzoyl derivatives. In these circumstances more concordant results were obtained.

Chloroacetyl derivatives. In these cases the technique was improved by using a small reaction flask (50 c.c.) with a long neck wrapped with compo tubing through which water was passed to act as a condenser. A narrow U-tube through which water was circulated was inserted down the neck, leaving room for the entrance of a pipette to remove samples without interrupting the heating. The higher b. p. of chloroacetic acid (185°) reduced chances of loss in these experiments. The solution was heated to boiling as rapidly as possible and timing started from the beginning of boiling. Samples were withdrawn at intervals into weighed flasks containing about 10 c.c. of water to cool the sample and stop the reaction : the flask was reweighed and its contents titrated. In these circumstances the results of independent determinations of k varied by from 3 to 7%, but we would not claim a reproducibility within 10%.

Benzoyl and substituted benzoyl derivatives. The experiments at the b. p. of xylene were carried out by the same method as for the chloroacetyl derivatives. The experiments at lower temperatures were carried out in a conical flask (100 c.c.) fitted with a cold-finger condenser immersed in an oil-bath controlled to ±0·1° (thermostat). The flask and solution were immersed in the thermostat for 10—15 minutes to reach the correct temperature. A sample (4 c.c.) was then withdrawn into a dry weighed flask cooled in ice, the flask was reweighed, 10—15 c.c. of water were added, and the acid was titrated. This titre was used to calculate the concentration at t_0, and further samples were withdrawn and titrated at intervals. The end points were much sharper in these cases. The results of separate determinations of k agreed to within about 10%. The following are details of one experiment, k being calculated from the equation $k = 2{\cdot}3[\log(1 - \alpha_0) - \log(1 - \alpha_t)]/(t - t_0)$:

0·805 *G. of benzoyl-α-*o*-methoxybenzaldoxime in* 21·26 *g. of xylene at* 120°.

t, secs.	Sample removed, g.	Titre, c.c. of 0·0201N-Ba(OH)$_2$.	α_t.	log $(1 - \alpha_t)$.	log $(1 - \alpha_0)$ − log $(1 - \alpha_t)$.	$k \times 10^5$, secs.$^{-1}$.
0	3·15	2·30	0·103	−0·047	—	—
600	3·06	5·43	0·249	−0·127	0·077	29·5
1200	3·14	8·51	0·381	−0·205	0·161	30·8
1800	3·13	10·88	0·488	−0·291	0·244	31·2
2400	3·10	12·93	0·586	−0·383	0·336	32·2
3000	3·18	15·05	0·665	−0·475	0·4128	32·8
3600	2·81	14·43	0·722	−0·556	0·509	32·6

Mean value : $k = 31{\cdot}4 \times 10^{-5}$ secs.$^{-1}$.

Effect of metals. The accelerating effect of copper was discovered when a copper, instead of a platinum, stirring-wire was used. Three experiments using acetyl-α-*m*-nitrobenzaldoxime (0·5 g.) in xylene in the presence of 0·005, 0·006, and 0·11 g. of finely divided copper (copper bronze) at 115° gave rate constants from 50 to 500 times those in the absence of copper, but in the limited number of experiments performed no correlation was observed between the rates and the amount of copper added. An experiment with benzoyl-α-benzaldoxime (0·5 g.) in the presence of 0·005 g. of copper at 120° and another at 115° showed rate constants approximately 100 times those without copper.

Mixtures of acetyl-α-3 : 4-methylenedioxybenzaldoxime, acetyl-α-*p*-dimethylaminobenzaldoxime, and finely divided copper, on heating for a few minutes to between 90° and 100°, decompose violently.

Mixtures of acetyl derivatives with finely divided silver, heated for some hours to 100°, or acetyl derivatives, heated in the presence of mercury, gave no indication of attack on the metal. Acetyl derivatives, boiled in xylene in the presence of calcium carbonate and copper, gave no evidence of the formation of copper salts.

Kinetic Measurements from the Evolution of Carbon Dioxide.—The carbethoxy- and diphenylcarbamyl-compounds decompose with the formation of unstable acids which break down to give carbon dioxide and alcohol or diphenylamine :

$$\mathrm{R{\cdot}CH{:}NO{\cdot}CO_2Et} \longrightarrow \mathrm{RCN} + \mathrm{HO{\cdot}CO_2Et} \longrightarrow \mathrm{CO_2} + \mathrm{EtOH}$$

$$\mathrm{R{\cdot}CH{:}NO{\cdot}CO{\cdot}NPh_2} \longrightarrow \mathrm{RCN} + \mathrm{HO{\cdot}CO{\cdot}NPh_2} \longrightarrow \mathrm{CO_2} + \mathrm{HNPh_2}$$

Measurement of this carbon dioxide was used as a means of determining the rate constant. The apparatus was a closed system consisting of a small flask surmounted by a condenser the upper end of which was connected *via* a rubber tube and tap manifold with a gas burette. This burette was jacketed, kept at a temperature constant to about ±½°, and provided with a suitable levelling device. The neck of the flask was surrounded by a vacuum jacket to maintain the temperature gradients constant where it emerged from the thermostat; the flask and condenser assembly was supported in a shaker, so that the mixture was constantly agitated.

The solvent xylene was freshly distilled into the flask for each experiment in a current of dry carbon dioxide to ensure its presaturation; when the flask had warmed to the temperature of the experiment enough carbon dioxide was evolved to fill the apparatus and displace the air initially present. A series of three reaction flasks of varying size (20, 30, and 80 c.c.) was used as it was found desirable to have as little dead space as possible, and the concentration of reactant was varied by using different amounts of solvent. The experiments were carried out by immersing the flask containing the solvent in the bath and allowing thermal equilibrium to be reached, as indicated by a steady burette reading when the flask was agitated. The seal between condenser and flask was momentarily broken for the insertion of the previously weighed sample in an open capsule, and the apparatus resealed with Faraday wax and fixed in the shaker. The burette had previously been set to zero, and readings of time and volume were then taken throughout the reaction.

In spite of the agitation the evolution of gas was still somewhat irregular and the final volume uncertain, so an adaptation of Guggenheim's method (*Phil. Mag.*, 1926, **2**, 538) was used to determine the rate constants. Readings were taken for approximately 6 times the half period of the reaction and from these a smoothed time–volume curve was drawn from which sets of readings B_1, B_2, . . . and B_1', B_2' . . . at times t_1, t_2, . . . and $t_1' = t_1 + T$, $t_2' = t_2 + T$ . . . respectively, could be obtained. The initial period immediately after the sample had been introduced, when steady conditions had not been reached and the rate of evolution of gas had not reached a maximum, was ignored; this generally covered the first 20% of the reaction. The value of the rate constant was then obtained from the equation, $2{\cdot}3 \log (B_{t'}' - B_t) = kt +$ constant by plotting the values of $\log (B_{t'}' - B_t)$ against t and measuring the slope of the straight line so obtained.

Details for one experiment are given below; variations between the values of the rate constant obtained from different experiments were not more than 10%.

0·340 *G. of carbethoxy-α-*m*-nitrobenzaldoxime in* 28·0 *g. of xylene at* 113·8°.

Time (mins.)	0	10	15	20	25	30	35	40	45	50	55
Burette reading (c.c.)...	0	1·9	2·8	3·8	4·7	5·5	6·2	6·8	7·6	8·4	9·2
Time (mins.)	60	65	70	75	80	85	90	95	100	105	
Burette reading (c.c.)...	9·9	10·6	11·3	11·9	12·6	13·2	13·8	14·4	15·0	15·5	
Time (mins.)	110	115	120	125	130	135	140	145	150	155	
Burette reading (c.c.)...	16·0	16·3	17·0	17·5	18·0	18·4	18·9	19·3	19·7	20·1	
Time (mins.)	160	165	170	175	180	185	190	195	200	205	
Burette reading (c.c.)...	20·5	20·9	21·3	21·7	21·9	22·4	22·6	23·0	23·3	23·4	
Time (mins.)	210	215	220	225	230	235	240	250	260	270	
Burette reading (c.c.)...	23·8	24·1	24·4	24·7	24·9	25·2	25·5	26·0	26·5	26·9	
Time (mins.)	280	290	300	310	320	330	340	350	360	370	
Burette reading (c.c.)...	27·3	27·5	27·9	28·3	28·6	28·8	29·0	29·2	29·5	29·3	
Time (mins.)	380	390	400	410	420	430	440	450	460	470	
Burette reading (c.c.)...	29·7	29·9	30·1	30·3	—	30·6	30·7	30·9	31·0	31·1	
Time (mins.)	480	490	500	510	525	540	555	570	585	600	
Burette reading (c.c.)...	31·3	31·3	31·4	31·4	31·4	31·5	31·6	31·7	31·8	31·7	

From the smoothed graph of the points given above the following values of B and B' were obtained, and hence $\log (B' - B)$:

t.	B.	t'.	B'.	$B' - B$.	$\log (B' - B')$.	t.	B.	t'.	B'.	$B' - B$.	$\log (B' - B)$.
15	2·8	315	28·4	25·6	1·408	165	20·9	465	31·1	10·2	1·009
30	5·4	330	28·8	23·4	1·369	180	22·0	480	31·2	9·2	0·964
45	7·7	345	29·2	21·5	1·332	195	23·0	495	31·3	8·3	0·919
60	9·8	360	29·4	19·6	1·292	210	23·9	510	31·4	7·5	0·875
75	11·9	375	29·7	17·8	1·250	225	24·7	525	31·5	6·8	0·833
90	13·8	390	30·0	16·2	1·210	240	25·5	540	31·6	6·1	0·785
105	15·6	405	30·2	14·6	1·161	255	26·3	555	31·6	5·3	0·724
120	17·0	420	30·4	13·4	1·127	270	26·9	570	31·7	4·8	0·681
135	18·6	435	30·6	12·0	1·079	285	27·4	585	31·8	4·4	0·644
150	19·7	450	30·9	11·2	1·049	300	28·0	600	31·9	3·8	0·580

Hence $k = 10{\cdot}3 \times 10^{-5}$ secs.$^{-1}$.

Subsidiary tests were made to determine the rate at which carbon dioxide is evolved from its supersaturated solution in xylene and these indicated that the rate is several hundred times that of the fastest reaction studied and would not therefore have any effect on the measurements. Besides the carbon dioxide there are also present in the apparatus xylene vapour and the alcohol formed in the reaction. As a result, from the condenser onwards the evolved gas is saturated with xylene and alcohol at the condenser temperature; this does not affect the calculation of the rate constant and may be allowed for in calculating the total volume of gas evolved. Agreement between the measured and calculated volumes of gas was not good, discrepancies amounting to as much as 20%; these may be due to dissolution of carbon dioxide in droplets of liquid formed on the walls of the condenser.

The decomposition of the fused compounds in the absence of solvent was carried out in a reaction flask consisting of a small bulb blown on the end of a B7 socket (Quickfit and Quartz) with an air-condenser consisting of a 7-inch length of 1-mm. capillary tubing on a B7 cone and connected to the gas-burette by rubber tubing. In these experiments a longer period elapsed before thermal equilibrium and the maximum rate of gas evolution were reached, because the flask and sample had to warm up from room temperature; with carbethoxy-*p*-dimethylaminobenzaldoxime (m. p. 116°) at 108° this period was 20 minutes, clearly because until then the material was not completely liquid; with the *p*-nitro-compound at 113·8° there was a sharp break in the plot of $\log (B' - B)$ against t caused by the eventual solidification of the material on formation of *p*-nitrobenzonitrile (m. p. 149°).

In conclusion we thank Mr. E. A. W. Hebdon for valuable help in connection with the apparatus for determining the carbon dioxide evolution, Mrs. B. A. Ambrose for the preparation of some of the compounds used, and the Central Research Fund of the University of London for a grant.

THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.
CHELSEA POLYTECHNIC, LONDON.

[*Received, October 7th,* 1949.]