[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO., EMERYVILLE, CALIF.]

# Thermal Decomposition of Acrolein. The Attack of Methyl and t-Butoxy Free Radicals on Acrolein

BY C. E. CASTRO<sup>1</sup> AND F. F. RUST

RECEIVED JUNE 29, 1961

The thermolysis of gaseous solutions of acrolein in the 500-600° region yields principally carbon monoxide, ethylene, propylene, hydrogen, methane, ethane, 1,3-butadiene and 1-butene in decreasing order of importance. The results are rationalized in part by a short chain decomposition of the aldehyde through vinyl radicals for which the unstable acrylyl fragment is a precursor. Studies of the methyl radical induced decomposition of acrolein at 250° in the gas phase and the *t*-butyl hypochlorite photochlorination of the aldehyde at 22° in solution allow rough approximations of  $k_{addition}/k_{abstraction}$  for methyl and *t*-butyl free radicals to be made. These estimates are 4 and 1/18 (max.), respectively.

#### Introduction

The literature abounds with the low temperature ionic chemistry of acrolein in solution. Very little attention, however, has been focused upon the high temperature behavior of this reactive aldehyde or upon its susceptibility toward free radical attack.

At 530°, in a static system, the decomposition of acrolein was found to yield: butylene, ethylene, carbon monoxide, methane, ethane and hydrogen. The kinetics of the reaction were complex.<sup>2</sup> The intermediacy of free radicals in the decomposition is suggested by the observation that the rate of consumption of acrolein at  $470^{\circ}$  was increased fourfold in the presence of ethylene oxide.<sup>3</sup>

More recently, di-*t*-butyl peroxide has been decomposed in acrolein vapor at both 134 and 169°.<sup>4</sup> The products identified were *t*-butyl alcohol, acetone, ethane, methane and carbon monoxide. These substances, except for carbon monoxide, are typically obtained from the decomposition of the peroxide in a variety of media<sup>5</sup> and thus provide no definite knowledge of the fate of the fragments derived from acrolein. The relatively high yields of carbon monoxide coupled with the small amounts of methane detected suggested that, at these temperatures, methyl radicals add to acrolein followed by polymerization of the aldehyde with the concerted loss of carbon monoxide at each propagation step.

 $R^{-} + CH_2 = CHCHO \longrightarrow RCH_2\dot{C}HCHO \longrightarrow$ 

 $CO + RCH_2\dot{C}H_2$  etc.

From the approximate constancy of the sum of the yields of acetone and *t*-butyl alcohol it was concluded that *t*-butoxy fragments do not add readily to acrolein.

We wish to report some results obtained from a study of the thermal decomposition of acrolein in the gas phase. In conjunction with this investigation we have determined the pattern of attack of methyl and *t*-butoxy free radicals on acrolein.

## Results and Discussion

The Thermal Decomposition of Acrolein.— Solutions of acrolein in toluene, benzene, cyclo-

(1) Department of Nematology, University of California, Riverside, Calif.

(2) H. W. Thompson and J. J. Frewing, J. Chem. Soc., 1443 (1985).
(3) C. J. M. Fletcher and G. K. Rollefson, J. Am. Chem. Soc., 58, 2135 (1936).

(4) D. H. Volman and R. K. Brinton, J. Cham. Phys., 20, 1764 (1952);
 D. H. Volman, Trans. Faraday Soc. Disc., 14, 253 (1953).

(5) J. H. Raley, F. F. Rust and W. E. Vaughan, J. Am. Chem. Soc., 70, 88 (1945); 70, 1336 (1945); E. R. Bell, F. F. Rust and W. E. Vaughan, *ibid.*, 72, 337 (1950); F. F. Rust, F. H. Senbold and W. E. Vaughan, *ibid.*, 72, 338 (1950). pentane and butadiene were thermolyzed in a flow system. The results obtained in the first three diluents were essentially the same; thus only those in toluene at  $600^{\circ}$  and benzene at  $500^{\circ}$  are reported in detail (Tables I and II). Although the general features of the butadiene-acrolein pyrolysis were similar to the others, the extreme complexity of the pyrolysate discouraged a quantitative analysis of its constituents.<sup>6</sup>

TABLE I

Products of the Decomposition of Acrolein in Toluene at  $600\,^\circ$ 

Mole ratio acrolein/toluene = 2.00; contact time, 4 sec. at  $600^{\circ}/1$  atm.

Moles reacted <sup><math>a</math></sup>	Run A	Run B
Acrolein	1.43	1.45
Toluene	0.19	0.067
% conversion of acrolein	41	47
Products	$\mathbf{Yield}, \mathbf{b} \ \mathbf{\%}$	
Carbon monoxide	86	97
Ethylene	22	24
Propylene	9.2	8.7
Hydrogen	7.2	8.3
Methane	5.4	6.2
Ethane	4.4	3.3
1,3-Butadiene	3.4	3.4
1-Butene	3.0	2.3

<sup>a</sup> Based on recovered starting material; more charring occurred in run A than in run B, although this was slight. <sup>b</sup> 100 (moles product/moles acrolein reacted).

#### TABLE II

Major Products of the Decomposition of Acrolein in  $$\rm Benzene^{a}$  at  $500\,^{\circ}$ 

Mole ratio acrolein/benzene = 2.00; contact time, 9.8 sec. at  $500^{\circ}/1$  atm.

		Mole reacted		
Acrolein	$0.41 \ (15.2\% \ conv.)$			
Benzenc	0.016			
Products	Vield, %	Products	Yield.	%
Carbon monoxide	100	1-Butene	3	
Ethylenc	20	1,3-Butadiene	2	
Propylene	12	Methane	2	
Ethane	3	Hydrogen	$^{2}$	
		Propane	2	

<sup>a</sup> As was the case in toluene, small amounts of other substances were obtained, but these were not investigated.

In addition to those substances listed in Table I, the following were detected in the pyrolysate in amounts of 1% or less: acetylene, propyne, pro-

(6) A fraction of the product having b.p.  $31.47^{\circ}$  was found to contain 18 components.

pane, *cis*- and *trans*-butene-2, *n*-butane, isoprene,  $C_5H_{10}$ , cyclohexene, dihydropyran, allylbenzene and a mixture of  $C_7$ -aldehydes.<sup>7</sup> The major products obtained from the pyrolysis of acrolein in benzene are listed in Table II.

These results are partially interpreted in terms of a short chain decomposition of acrolein through vinyl radicals for which the acrylyl radical is a precursor. The initiation step is presumed to be that indicated by analogy with other aldehyde decompositions.<sup>8</sup>

$$CH_2 = CHCHO \longrightarrow CH_2 = \dot{C}H + \dot{C}HO$$

$$CH_2 = \dot{C}H + CH_2 = CHCHO \longrightarrow$$

$$CH_2 = CH_2 + CH_2 = CH\dot{C} = CH\dot{C}$$

$$CH_2 = CH\dot{C} = O \longrightarrow CO + CH_2 = \dot{C}H$$

$$CH_2 = \dot{C}H + CH_2 = CH_2 \longrightarrow CH_2 = CHCH_2\dot{C}H_2$$

$$CH_2 = CHCH_2\dot{C}H_2 + CH_2 = CHCHO \longrightarrow$$
  
 $CH_2 = CHCH_2CH_1 + CH_2 = CH\dot{C} = O$ 

$$2CH_{2} = \dot{C}H \longrightarrow CH_{2} = CHCH = CH_{2}$$

At the higher temperature hydrogen atoms might also function as chain carriers.

$$\dot{C}HO \longrightarrow H + CO$$

$$H + CH_2 = CHCHO \longrightarrow H_2 + CH_2 = CH\dot{C} = O$$

The suggested scheme of decomposition is consonant with the findings of recent studies of the photolysis of acrolein<sup>9</sup> and is in accord with the results of the methyl radical induced decomposition of acrolein presented later. The presence of allylbenzene in the pyrolysate supports the intermediacy of vinyl radicals.<sup>10</sup>

 $CH_2 = \dot{C}H + C_6H_5\dot{C}H_2 \longrightarrow C_6H_3CH_2CH = CH_2$ 

Additional evidence for the free radical nature of the decomposition and for the participation of vinyl fragments was obtained by a cursory examination of the reaction in the presence of oxygen.

A 2:1 mixture of acrolein and  $air^{11}$  thermolyzed at 500° for 10 sec. afforded no oxygenated derivatives of acrolein. All oxygen was consumed and no carbon dioxide was evolved. Under these conditions, which are identical to those of the acroleinbenzene pyrolysis, 84.2% of the aldehyde had dissipated. Moreover, along with the products typical of the decomposition in other media, the oxygencatalyzed reaction led to the production of acetaldehyde and water.

$$CH_{2} = \dot{C}H + O_{2} \longrightarrow CH_{2}CHOO \xrightarrow{i} acrolein \\ CH_{2} = CHOOH \longrightarrow CH_{2} = CHO + HO \xrightarrow{i} acrolein \\ CH_{2} = CHOOH \longrightarrow CH_{2} = CHO + HO \xrightarrow{i} acrolein \\ CH_{3}CHO + H_{2}O$$

The majority of the trace quantities present in the acrolein pyrolysate are compatible with the proposed scheme of decomposition and can be ration-

(7) Cyclohexene-3-carboxaldehyde and others of uncertain structure.

(8) E. W. F. Steacie, "Atomic and Free Radical Reactions," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1954, pp. 206-219, and references therein.

(9) A. G. Harrison and F. P. Lossing, Can. J. Chem., 1696 (1959);
 D. H. Volman, P. A. Leighton, F. E. Blacet and R. K. Brinton, J. Chem. Phys., 18, 205 (1950).

(10) No bibenzyl was found. The very small conversion of toluene indicates that hydrogen abstraction from acrolein is more rapid than from toluene.

(11) Mole ratio acrolein/ $O_2 = 9.4$ ,

alized in terms of well-known free radical pathways.<sup>12</sup> Clearly, the relatively high yields of propylene *are not accommodated* by the proposed mechanism, nor are the other odd-numbered carbon products. Moreover, the secondary decomposition of butene-1<sup>13</sup> or ethylene<sup>14</sup> cannot be invoked to explain these results, since these substances were not found to be appreciably decomposed, even under more drastic conditions than those of the acrolein thermolysis. Thus, at this time, it remains possible that other modes of decomposition of acrolein<sup>15</sup> may be important at these temperatures, and that the above findings might also result from the decomposition of non-detected unstable intermediates.<sup>16</sup>

The Attack of Methyl Radicals on Acrolein.— Acrolein was subjected to an environment swamped with methyl radicals at 250° for 20 sec.<sup>17</sup> (eleven half-lives of di-*t*-butyl peroxide) in a flow system. The results are presented in Table III.

These data lend support to the suggested mechanism of decomposition of acrolein at higher temperatures, and they allow an estimation of the relative importance of methyl addition to acrolein as compared to hydrogen abstraction.

Methyl radicals result from decomposition of the peroxide.<sup>4</sup> The higher temperature employed favors the collapse of t-butoxy to acetone and methyl.

$$\begin{array}{cccc} CH_3 & CH_3 & CH_3 \\ CH_3C-O- & O-CCH_3 \longrightarrow 2 CH_3C-O \\ & & & & \\ CH_3 & CH_3 & CH_3 \\ & & & CH_3 \end{array} \xrightarrow{O}_{2CH_3CCH_3 + 2\dot{C}H_3}$$

The material balance for di-*t*-butyl peroxide taken from Table III is: di-*t*-butyl peroxide = 1/2 (acetone + *t*-butyl alcohol); found:  $0.65 \cong 0.62$ . Thus it is valid that the number of moles of methyl radicals produced equals the number of moles of acetone detected.

(12) The cyclic olefins are interesting in that although they may result from a thermal Diels-Alder reaction (the high temperature is certainly unfavorable to this process; cf. F. O. Rice, P. M. Ruoff and E. L. Rodowskas, J. Am. Chem. Soc., **60**, 955 (1938); they can also be rationalized as radical addition-cyclization products. Thus, cyclohexene might arise via

$$\begin{array}{c} CH_{2}=\dot{C}H + CH_{2}=CHCH=CH_{2} \rightarrow \\ \hline \\ CH_{2}=CHCH_{2}\dot{C}HCH=CH_{2} \\ \downarrow \\ CH_{2}=CHCH_{2}CH=CH\dot{C}H_{2} \end{array} \rightarrow \begin{array}{c} & & \\ &$$

Cf. L. M. Porter and F. F. Rust, J. Am. Chem. Soc., 78, 5571 (1956).
(13) The thermal dissociation of butene-1 to methyl and allyl radicals has been reported; A. H. Sehon and M. Szwarc, Proc. Roy. Soc. (London), A202, 263 (1950); J. Chem. Phys., 18, 237 (1950).

(14) For a review of the thermal decomposition and polymerization of ethylene, cf. ref. 8, pp. 175-183.

 $(15)\,$  For example, a direct dissociation of a crolein to methylene and carbon monoxide.

(16) The addition of vinyl radicals to acrole in should yield  $\omega$ -pentenal which might be expected to cleave to allyl and formylmethyl radicals in a manner analogous to the cleavage of 1,5-hexadiene; W. A. Bryce and D. J. Ruzicka, *Can. J. Chem.*, **38**, 835 (1960); and unpublished results of the authors.

(17) At temperatures below 400° the decomposition of acrolein is slow. The pure aldehyde at 350° for 1.6 min. remained intact. At 180° for one half-life of di-*d*-butyl peroxide (5%) only small amounts of disacryl polymer were found.

Methyl radicals are consumed by the paths

$$k_{addn}$$

1

 $CH_3 + CH_2 = CHCHO$ 

$$\sqrt{k_{abst}}$$

$$CH_4 + CH_2 = CH\dot{C} = 0 \longrightarrow CO + CH_2 = \dot{C}H \text{ etc}$$

$$\dot{C}H_3 + CH_2 = \dot{C}H \longrightarrow CH_2 = CHCH_3$$

$$CH_3 + CH_2 = CH - CH_3 \longrightarrow CH_3CH_2\dot{C}HCH_3 \xrightarrow{\dot{C}H_3}$$

CH:

$$\dot{C}H_{3} + CH_{2} \longrightarrow CH_{3}CH_{2}\dot{C}H_{2} \xrightarrow{\dot{C}H_{3}} CH_{3}CH_{2}CH$$

If the most prevalent radicals in the system abstract hydrogen from acrolein, and if the resulting acrylyl fragment rapidly decomposes

## TABLE III

# PRODUCTS FROM THE METHYL RADICAL INDUCED DECOMPO-SITION OF ACROLEIN AT 250°

Charged: di-t-butyl peroxide, 0.646 mole; acrolein, 1.93 moles; contact time, 20 sec. at 250°/1 atm.; moles acrolein reacted, 0.258,ª 13.4% conversion.

Products	Moles		
Acetone	1.23		
Ethane	0.39		
2-Methylbutyraldehyde	.096		
Carbon monoxide	$.068 \pm 0.004$		
Methane	.060		
Propylene	.016		
<i>t</i> -Butyl alcohol	.012		
1-Butene	.011		
Ethylene	.0075		
Isopentane	.0043		
2,3-Dihydro-4H-pyranyl-			
2-carboxaldehyde	.0033		
Propane	.0017		
1,3-Butadiene	.0010		
<i>n</i> -Butane	,0006		
2-Butene	.0005		

" The weight of acrolein not accounted for by the listed products is 4.5 g. From the pyrolysate there was obtained a heavy non-distillable oil and a very high boiling fraction (presumably low mol. wt. polymers of acrolein which contained only a small number of carbonyl groupings) together amounting to 5.3 g.

The Attack of t-Butoxy Radicals on Acrolein.-

Although evidence for the transient existence of

acrylyl fragments in the gas phase decompositions

of acrolein at higher temperatures seems quite

compelling, no products of these decompositions

could be detected that might be considered to di-

rectly result from an acrylyl precursor. The elusive

nature of these species in the gas phase suggested

that they might be captured at low temperatures in solution. The problem is compounded, however, by the easy polymerization of acrolein.<sup>19</sup> In light of

the propensity of t-butoxy radicals for allylic hydro-

gen abstractions<sup>20</sup> and the effectiveness of t-butyl

hypochlorite<sup>21</sup> as a chlorine transfer agent, it was

hoped that the hypohalite might provide a vehicle for both generating and trapping acrylyls<sup>22</sup> in solu-

This expectation was fully confirmed by exam-

ining the photolysis of a dilute solution of acro-

$$\begin{array}{c}
\overset{CH_{3}}{\leftarrow} + CH_{2} = CHCHO \longrightarrow CH_{4} + CH_{2} = CH\dot{C} = O \\
\overset{CH_{3}}{\leftarrow} & CH_{3} \\
\overset{I}{\leftarrow} CH_{3}CO + CH_{2} = CHCHO \longrightarrow CH_{3}COH + CH_{2} = CH\dot{C} = O \\
\overset{I}{\leftarrow} & CH_{3} \\
\overset{I}{\leftarrow} CH_{3} & CH \\
CH_{2} = \dot{C}H + CH_{2} = CHCHO \longrightarrow CH_{2} = CH_{2} + CH_{3} = CH\dot{C} = O
\end{array}$$

then  $CO = CH_4 + CH_2 = CH_2 + t$ -BuOH; found:  $0.068 \pm 0.004 = 0.060 + 0.0075 + 0.012 = 0.079$ or using the upper limit for CO:  $0.072 \approx 0.079$ . The agreement is within the experimental error.<sup>18</sup>

These results confirm the short chain decomposition of acrolein through vinyl radicals and they attest to the instability of acrylyl noted above. This instability is further manifested in the lack of methyl vinyl ketone amongst the products.

$$CH_2 = CH\dot{C} = O + \dot{C}H_3 \longrightarrow CH_2 = CH\ddot{C}CH_3$$

In fact, loss of carbon monoxide from acrolein may occur concomitantly with hydrogen abstraction at these temperatures.

$$\dot{R}$$
 + CH<sub>2</sub>=CHCHO ---> RH + CO + CH<sub>2</sub>= $\dot{C}H$ 

The relative importance of addition to acrolein and hydrogen abstraction from the aldehyde by methyl radicals may be estimated from the expression kaddn

$$\frac{k_{abst}}{k_{abst}} \cong$$

±6%.

≚ 0 CH: CH<sub>3</sub>  $\underline{CH_3CCH_3} - (\underline{CH_4} + \underline{CH_3CH_2CHCHO} + \underline{CH_2} = \underline{CHCH_3} + 3\underline{CH_3CH_2CHCH_3} + 2\underline{CH_3CH_2CH_2CH_3} + \underline{CH_2CH_3} + \underline{CH_2CH_3} + 2\underline{C_2H_6})$ CH₄

tion.

Employing the data of Table III,  $k_{addn}/k_{abst} \cong 4$ . Thus, at 250° methyl radicals predominantly add to acrolein, as Volman and Brinton observed at lower temperatures.<sup>4</sup>

(18) The relative error in yield of all products being approximately

(19) Thus, in our hands, both the succinimidyl and benzyloxy radicals rapidly polymerized dilute solutions of acrolein.

(20) C. Walling, "Free Radicals in Solution," John Wiley and Sons. Inc., New York, N. Y., 1957, Chapter 10, and references therein. (21) C. Walling and B. B. Jacknow, J. Am. Chem. Soc., 82, 6108,

6113 (1960).

(22) The conversion of benzaldehyde to benzoyl chloride by tbutyl hypochlorite has been noted; D. Ginsburg, ibid., 73, 702 (1951). lein and *t*-butyl hypochlorite in carbon tetrachloride at 22° in the presence of sodium carbonate. The results are summarized in Table IV.

#### TABLE IV

PRODUCTS OF THE ACROLEIN-*t*-BUTYL HYPOCHLORITE Photolysis in Carbon Tetrachloride at 22°

Reactants	Mole	Productsb	$\mathbf{N}$	Iole
<i>i</i> -Butyl hypochlorite Acrolein Sodium carbonate	0.202 <sup>a</sup> .404 .20	t-Butyl alcohol Acetone t-Butyl acrylate Acrolein recovered	0,151 .015 ,026 .126	(max.)

 $^a$  0.505 molar.  $^b$  In addition a small amount of acrolein polymer was obtained.

The consumption of hypochlorite was complete and no gas was evolved. From a consideration of the reactions

$$t-Bu\dot{O} \longrightarrow CH_{3} + CH_{3}CCH_{4}$$

$$CH_{2}=CH\dot{C}=O + t \cdot BuOC1 \longrightarrow CH_{2}=CHCC1 + t \cdot Bu\dot{O}$$

$$CH_{2}=CHCC1 + t \cdot BuOH \xrightarrow{Na_{2}CO_{3}} CH_{2}=CHCOt \cdot Bu$$

we have estimated  $k_{addn}/k_{abst}$  by utilizing the expression

$$\frac{k_{\mathrm{addn}}}{k_{\mathrm{abst}}}\cong$$

t-Bu

t-butyl hypochlorite -

(acetone + t-butyl alcohol + t-butyl acrylate) t-butyl alcohol + t-butyl acrylate

to be 1/18. This value is at best a maximum of  $k_{addn}/k_{abst}$ , but it suffices to demonstrate that *t*-butoxy radicals predominantly abstract the aldehydic hydrogen of acrolein. This result is to be contrasted with the preponderant addition of *t*-butoxy radicals to butadiene<sup>23</sup> and the photoaddition of *t*-butyl hypochlorite to bicycloheptadiene.<sup>24</sup>

#### Experimental

Materials.—Shell acrolein was fractionated through a 61cm. Vigreux column. A middle cut was taken having b.p.  $52-52.5^{\circ}$ ,  $n^{20}$ D 1.4000. The material was inhibited with hydroquinone (0.3 g./500 g. of acrolein) and stored in the refrigerator under nitrogen in a brown bottle. The initial smaller scale pyrolysis runs in which freshly distilled uninhibited acrolein was employed established that the small amounts of hydroquinone present in the latter studies did not noticeably affect the course of the reaction. J. T. Baker "analyzed reagent" grade benzene was used without further purification. Mallinckrodt toluene was distilled from potassium, b.p. 110.5°. Shell Chemical di-*t*butylperoxide was used without purification. *t*-Butyl hypochlorite was prepared and purified according to Teeter and Bell<sup>26</sup>; b.p. 78°. **Pyrolyses Techniques.**—All pyrolyses were performed in a

**Pyrolyses Techniques.**—All pyrolyses were performed in a flow system. The reactor employed for the 600° work was composed of a Vycor tube snugly fitted into a Hastelloy B. jacket. The volume of the reactor was 41.0 ml. and its inside diameter was 1.07 cm. Premixed reactants were admitted first to a small preheater at 250°. A Pyrex reactor was employed for all other work.<sup>26</sup> The Pyrex reactor was equipped with dual spiral inlet "preheater" tubes. The reaction chamber had a volume of 610 ml. Temperatures were maintained by a heavy duty furnace connected through a Celectray to four iron-constantan thermocouples which were spaced evenly along a well down the center of the reactors. The temperature was marked at *ca*. 20-sec. interval sweeps on a Brown recorder.

Liquid reactants were premixed in an addition funnel and pressured into the system with dry nitrogen. The flow rate was controlled by a Whitey No. 00 needle valve.

The effluent was passed through a spiral condenser connected to a flask immersed in an ice-water-bath which was in turn connected to two ice-water traps, a wet test meter, calcium chloride and potassium hydroxide drying towers, the sampling tube, and two CO<sub>2</sub> or liquid N<sub>2</sub> cooled traps, the last of which was fitted to a drying tube.

Gaseous samples were analyzed mass spectrometrically and by gas-liquid chromatography (g.l.c.) employing a 15-m. 6-mm. dimethyl sulfolane on firebrick column at 40 or 0°. Orsat analyses for carbon monoxide checked well with those obtained by the mass spectrometer. The liquid pyrolysate to which hydroquinone was added was fractionated under nitrogen through a 61-cm. glass helices packed column.

nitrogen through a 61-cm. glass helices packed column. The Acrolein-Toluene Pyrolysis.—All liquid fractions were analyzed by g.l.c. on a 1.8-m. 6-mm. DC-710 on firebrick column; g.l.c. analyses of a fraction b.p. 58-64° (20 mm.) on di-isodecyl phthalate indicated the presence of allyl-benzene. A portion of this fraction was separated on a large DC-710 trapping column. The blip corresponding to allylbenzene had an infrared spectrum identical with authentic material. The other constituents of this fraction were C<sub>r</sub>-aldehydes. The infrared spectrum of the mixture indicated the presence of an  $\alpha_{\beta}$ -unsaturated carbonyl.

In one run the final CO<sub>2</sub> trap contents were treated with excess bromine at 0°. There was obtained 1,2,3,4-tetrabromobutane, m.p. 117° (lit. 118°) and 1,2-dibromopropane  $n^{20}$ D 1.5192 (lit. b.p. 142°,  $n^{20}$ D 1.5193). The Di-t-butyl Peroxide-Acrolein Pyrolysis at 250°.—The

The Di-t-butyl Peroxide-Acrolein Pyrolysis at 250°.—The gaseous products were analyzed as outlined above. Fractionation of the pyrolysate yielded seventeen fractions (b.p.  $37^{\circ}$  (1 atm.) -91° (18 mm.)). All fractions were subjected to g.l.c. analyses on 1.8-m. 6-mm. triethylene glycol and  $\beta$ , $\beta'$ -oxydipropionitrile columns. From a fraction having b.p. 81-86.5°, a semicarbazone m.p. 95-96° and a 2,4-dinitrophenylhydrazone m.p. 126-127° were prepared.

Anal. Caled. for  $C_{11}H_{14}N_{4}O_4$ : C, 49.6; H, 5.3; N, 21.0. Found: C, 49.8; H, 5.2; N, 20.9.

A mixture melting point of the above dinitrophenylhydrazide with authentic 2-methylbutyraldehyde<sup>27</sup> dinitrophenylhydrazide was undepressed, *i.e.*, m.p. 126-127°. The *t*-Butyl Hypochlorite Chlorination of Acrolein.—A

The t-Butyl Hypochlorite Chlorination of Acrolein.—A 500-ml. flask fitted with a thermometer and a condenser connected to a calcium chloride tube was charged with 22 g of t-butyl hypochlorite (0.202 mole), 400 ml. of carbon tetra-chloride, 22.7 g. of acrolein (0.404 mole) and 21 g. of anhydrous sodium carbonate (0.20 mole). The flask was thermostated at  $20-22^{\circ}$  and irradiated with three 200-watt light bulbs for 23 hr. Two of the bulbs were immersed in the bath and one was without. The faintly yellow solution obtained in this manner gave no KI test. The inorganic salts were filtered off and the solution was distilled through a 0.5-m. helices packed column. The vacuum distillation was accomplished in a small Vigreux. Each fraction was subjected to vapor phase chromatographic analysis on first a 1.8-m. 6 mm. triethylene glycol column on firebrick and then on a similar  $\beta_{\beta}\beta'$ -oxydipropionitrile column. The triethylene

<sup>(23)</sup> D. H. Volman and W. M. Graven, J. Am. Chem. Soc., 74, 3111 (1953).

<sup>(24)</sup> The authors have found that dilute solutions of *t*-butyl hypochlorite and bicycloheptadiene in carbon tetrachloride upon photolysis provided high yields of 3-*t*-butoxy-5-chlorotricyclo[2.2.1.0] heptane and no products resulting from hydrogen abstraction. Similar results have been reported recently, J. Org. Chem., 26, 287 (1961).

<sup>(25)</sup> H. M. Teeter and E. W. Bell, Org. Syntheses, 37, 20 (1952).

<sup>(26)</sup> That is, at 500° and below.

<sup>(27)</sup> Prepared from 2-methylbutanol by dichromate oxidation.

glycol column resolved carbon tetrachloride, t-butyl alcohol and t-butyl acrylate from a mixture of acrolein and acetone. The acrolein-acetone pair was resolved on  $\beta$ ,  $\beta'$ -oxydipropionitrile. The blip corresponding to t-butyl acrylate was trapped ten times from the triethylene glycol column. Its infrared spectrum was identical with the spectrum of authentic gaseous t-butyl acrylate.28

Acknowledgment.—The authors are indebted to Mr. F. L. Rodgers for patient assistance with the experimentation.

(28) This substance was prepared in poor yield from acrylyl chloride and t-butyl alcohol in the presence of Na<sub>2</sub>CO<sub>8</sub>; b.p. 56° (80 mm.), n D 20.5 1.4102.

[CONTRIBUTION FROM THE DOW CORNING CORPORATION, MIDLAND, MICH.]

# The Effect of Polar Substituents on the Acid-catalyzed Hydrolysis of Organosilicon Hydrides

# BY OMAR W. STEWARD AND OGDEN R. PIERCE

RECEIVED JULY 19, 1961

The first-order rate constants for the acid-catalyzed hydrolysis of sixteen fluoroalkyl-,  $\omega$ -cyanoalkyl- and *n*-alkylsilicon hydrides have been determined using aqueous ethanolic hydrochloric acid (1.43 N, 95 vol.-% ethanol) at 34.8°. The firstorder rate constants are correlated using the Taft equation. The correlations are discussed in terms of polar effects, steric effects and dative  $\pi$ -bonding.

#### Introduction

The polar effect of substituted alkyl groups on the alkali-catalyzed hydrolysis of triorganosilicon hydrides has been reported previously.<sup>1</sup> An excellent correlation of the second-order rate constants was obtained using the Taft equation<sup>2</sup> for triorganosilicon hydrides containing fluoroalkyl,  $\omega$ cyanoalkyl and n-alkyl groups.<sup>1a</sup>

Other linear relationships involving the inductive effect of substituent groups in silicon hydrides have been reported: (a) Hammett's  $\sigma$ -values and modified  $\sigma$ -values vs. log k for the base-catalyzed hydrolysis of triorganosilanes,<sup>3</sup> (b)  $\nu$  SiH (cm.<sup>-1</sup>) vs. empirically determined E-values and Taft's  $\sigma^*$ -values,<sup>4</sup> (c)  $\nu$  SiH (cm.<sup>-1</sup>) vs.  $\tau$  (p.p.nl.) for a proton attached to silicon.<sup>5</sup> (d)  $\nu$  SiH (cm.<sup>-1</sup>) vs. log K (25°) for the hydrolysis of triorganochlorosilanes.6

The acid-catalyzed solvolysis of organosilicon hydrides has been studied by Taketa, et  $al_{.,7}$  and Baines and Eaborn.<sup>8</sup> In this paper a study is reported on the effect of polar substituents on the acid-catalyzed hydrolysis of mono-, di- and tri-organosilicon hydrides. The first-order rate constants are correlated using the Taft equation. The correlations are discussed in terms of polar effects, steric effects and dative  $\pi$ -bonding.

## Experimental

Starting Materials .- Trichlorosilane, 3,3,3-trifluoropropyltrichlorosilane,<sup>9</sup>β-trichlorosilylpropionitrile,<sup>10,11</sup>β-metlyl-

(1) (a) O. W. Steward and O. R. Pierce, J. Am. Chem. Soc., 83,

1916 (1961); (b) 81, 1983 (1959).
(2) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 556-675.

(3) (a) H. Gilman and G. E. Dunn, J. Am. Chem. Soc., 73, 3404 (1951); (b) G. Schott and C. Harzdorf, Z. anorg. n. allgem. Chem., 306, 180 (1960)

(4) (a) A. L. Smith and N. C. Angelotti, Spectrochim. Acta, 15, 412 (1959); (b) H. W. Thompson, *ibid.*, **16**, 238 (1960).

(5) D. E. Webster, J. Chem. Soc., 5132 (1960).

(6) J. F. Hyde, P. L. Brown and A. L. Smith, J. Am. Chem. Soc., 82, 5854 (1960).

(7) A. Taketa, M. Kumada and K. Tarama, Bull. Inst. Chem. Research, Kyoto Univ., 31, 260 (1953).

(8) J. E. Baines and C. Raborn, J. Chem. Soc., 1436 (1956).

(9) P. Tarrant, G. W. Dyckes, R. Dunmire and G. B. Butler, J. Am. Chem. Soc., 79, 6536 (1957).

dichlorosilylpropionitrile,10,11 chloromethyldimethylchlorosilane<sup>12</sup> and 3-bromo-1,1,1-trifluoropropane<sup>13</sup> were available in research quantities. They were fractionally distilled before being used.

Preparation of 3,3,3-Trifluoropropyl-n-butyldiethoxysilane Bis-(3,3,3-trifluoropropyl)-diethoxysilane.—Absolute and ethanol (194 g., 4.2 moles) was added to 3,3,3-trifluoro-propyltrichlorosilane (463 g., 2.0 moles) over a period of 0.5 hour. Throughout the addition the reaction temperature was maintained between  $50-60^\circ$ . After addition was complete, the mixture was heated to 120° and al-lowed to cool to room temperature. The reaction mixture was then stirred for 16 hours with a slow nitrogen sweep to remove any remaining hydrogen shifts. to remove any remaining hydrogen chloride. The material in the flask, 3,3,3-trifluoropropylethoxychlorosilanes (493 g.), analyzed for one chlorine per silicon, a 98% yield.

Anal. Caled. for C7H14ClF3O2Si: Cl, 14.15. Found: Cl, 14.4.

n-Butylmagnesium bromide, dissolved in ether (550 ml.), prepared from n-butyl bromide (116 g., 0.85 mole) and magnesium (20.7 g., 0.85 mole), was added to the above prepared 3,3,3-triffuoropropylethoxychlorosilanes (213 g., 0.85 mole), dissolved in ether (200 ml.), over a period of 0.5 hour. Throughout the addition the reaction mixture was cooled in an ice-bath. After refluxing for 16 hours, the reaction mixture was poured onto a mixture of cracked ice and sodium bicarbonate (212 g., 2.0 moles). The ether layer was washed and dried over anhydrous calcium sulfate. After removing the ether, fractional distillation gave: 3,3,3trifluoropropyltriethoxysilane<sup>14</sup> (33.5 g., 0.13 mole), b.p. 82° (30 mm.),  $n^{25}$ D 1.3650, a 15% yield; 3,3,3-trifluoropropyl-*n*-butyldiethoxysilane (146 g., 0.54 mole), b.p. 105° (30 mm.),  $n^{25}$ D 1.3858,  $d^{25}$ , 0.991, a 63% yield.

Anal. Caled. for  $C_{11}H_{23}F_3O_2Si$ : C, 48.5; H, 8.51; F, 20.9. Found: C, 49.0; H, 8.65; F, 21.1.

3,3,3-Trifluoropropyldi-n-butylethoxysilane (5.3 g., 0.019 mole), b.p. 126.5° (30 mm.),  $n^{25}$ D 1.4073,  $d^{25}$ , 0.944, a 2% vield.

Anal. Calcd. for  $C_{13}H_{27}F_3OSi: C, 54.9; H, 9.57; F, 20.0.$  Found: C, 55.8; H, 10.1; F, 19.9.

Using the same procedure described above, 3,3,3-trifluoropropyImagnesiumi bromide, dissolved in ether (500 nil.), prepared from 3-bromo-1,1,1-trifluoropropane (150 g., 0.85 mole) and magnesium (20.7 g., 0.85 mole), was added to the 3,3,3-trifluoropropylethoxychlorosilanes (213 g., 0.85 mole). Fractional distillation gave: 3,3,3-trifluoropropyltriethoxysilane<sup>14</sup> (15.4 g., 0.06 mole), b.p.

(10) J. C. Saam and J. L. Speier, J. Org. Chem., 24, 427 (1959).

(11) G. D. Cooper and M. Prober, ibid., 25, 240 (1960). (12) R. H. Krieble and J. R. Elliott, J. Am. Chem. Soc., 67, 1810 (1945).

(13) P. Tarrant, A. M. Lovelace and M. R. Lilyquist, ibid., 77, 2783 (1955).

(14) O. W. Steward and O. R. Pierce, J. Org. Chem., 26, 2943 (1961).