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The Energy of the C-H Bond in the Fluoro-Toluenes

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The pyrolysis of the three fluoro-toluenes was investigated, and it was shown that the mechanism of the decomposition is the same as suggested previously for the decomposition of toluene and the xylenes. The experimental results prove that the C-H bond energy in all fluoro-toluenes is nearly the same as the C-H bond energy in toluene, i.e., about 78 kcal./mole, thus showing that the field effect has very little influence on the bond energy. This conclusion definitely establishes the presence of hyperconjugation for para-xylene as the cause of the weakening of the C-H bond in the CH_3 groups. The difference in the effects of dipoles on ionic and radical reactions is pointed out.

THE investigation of the pyrolysis of toluene and the xylenes¹ has revealed that these processes are homogeneous, unimolecular gas reactions. Their rate determining step is the dissociation of the hydrocarbon into a benzyl (or xylyl) radical and a hydrogen atom, and the latter reacts with the excess of hydrocarbon producing either H₂ or CH₄. The unimolecular rate constant (measured by the quantity of H₂+CH₄ produced) is given by

$$k_u = \gamma \cdot e^{-E/RT},$$

where γ has a value of the order $2 \cdot 0.10^{13}$ -2.5.10¹³ for toluene, and twice as much for xylenes (because of the statistical factor 2), and *E* is the bond energy of the C-H bond in the methyl group.*

In further pursuit of this investigation we have now measured the rates of pyrolysis of the three fluoro-toluenes and compared them to the rate of pyrolysis of toluene. We hoped that this might reveal the effect which the fields of the dipoles have on the energy of C-H bonds.

We shall assume as the first approximation that the value of γ remains the same for the k_u of the pyrolysis of all substituted toluenes.**,²⁻⁴ On this basis the change in the C – H bond energy caused by substitution can be calculated from the ratio of k_u of the pyrolysis of the substituted toluene to the k_u obtained for the pyrolysis of toluene itself at the same temperature.

EXPERIMENTAL

The apparatus and the technique have been described by one of us in a previous paper.¹ In the present work the reaction vessel and the furnace were changed slightly, thus improving the temperature distribution and reducing its variations in the reaction vessel from $\pm 2^{\circ}$ C to $\pm 1^{\circ}$ C. The reinvestigation of the pyrolysis of toluene gave the same products and in the same proportions as reported previously,¹ while the individual values for k_u were about 5 percent lower than in the earlier experiments. This small discrepancy is most probably due to the somewhat arbitrary method of fixing on a particular value for the temperature of the reaction-in view of the temperature gradient-and also to some uncertainty in estimating the volume of the reaction vessel. Such errors are, of course, eliminated in comparing the k_u for various similar compounds measured in the same apparatus as we do in this paper.

The fluoro-toluenes were prepared by the method of Balz and Schiemann⁵ (through the tolyl-diazonium fluoborates) and purified by

¹ M. Szwarc, J. Chem. Phys. 16, 128 (1948).

^{*} It is assumed that the recombination of the benzyl radical and the H atom does not involve any activation energy, and therefore the energy of activation for the dissociation process is equal to the heat of dissociation, i.e., to the C-H bond energy. ** A review of the literature (see references 2 and 3) shows

^{**} A review of the literature (see references 2 and 3) shows that in various reactions the substitution in para- or metaposition of the benzene ring causes but slight change in the entropy of activation. This seems to be true even in the case of ortho substitution by *F* atom (see reference 4). ² E. G. Williams and C. N. Hinshelwood, J. Chem. Soc.

^{1079 (1934),}

³C. K. Ingold and W. S. Nathan, J. Chem. Soc. 222 (1936).

⁴ D. P. Evans, J. J. Gordon, and H. B. Watson, J. Chem. Soc. 1430 (1937).

⁶ G. Balz and G. Schiemann, Ber. **60**, 1188 (1927); *ibid.*, **62**, 1798 (1929),

TABLE Ia.

			Extrapolated to T = 1077°K						
		%	ku •10) ³ k	1077 ·103	kı	077		
Run	т∘к	Decomp.	sec	L	sec.⁻¹	Average	k toluene	Remarks	
Tolu	ene								
1	1082	0.180	4.8	3.8	1	0.99			
2	1082	0.168	4.5	3.6		0.95			
3	1081	0.167	4.4	3.7	ļ	0.97			
5	1080	0.161	4.3	3.8	average	0.99			
6	1080	0.165	4.4	3.Š	for	1.02			
26	1075	0.084	3.4	3.6	₹1077°K	0.95			
27	1073	0.088	3.5	3.9	3.81	1.02			
28	1070	0.082	3.2	4.0		1.05			
29	1071	0.084	3.3	3.9	1	1.02			
30	1072	0.086	3.4	3.9	J	1.02			
Para	fluor	o-toluene	2						
7	1080	0.158	4.0	3.5		ן 0.92		not pyrolyzed	
8	1082	0.159	4.0	3.3		0.87		not pyrolyzed	
12	1084	0.161	4.2	3.2		0.84		once pyrolyzed	
13	1090	0.210	5.4	3.4		0.89 La	average	once pyrolyzed	
14	1077	0.105	3.6	3.6		0.95 ſ	0.906	not pyrolyzed	
15	1078	0.098	3.5	3.4		0.89		not pyrolyzed	
16	1080	0.108	3.9	3.5		0.92		not pyrolyzed	
18	1076	0,102	3.6	3.7		0.97		once pyrolyzed	
Meta	a-fluo	ro-toluen	e						
20	1079	0.095	3.5	3.2		0.84		not pyrolyzed	
22	1078	0.090	3.3	3.1		0.81 (average	once pyrolyzed	
23	1076	0.082	3.0	3.0		0.79 (0.812	once pyrolyzed	
24	1078	0.086	3.3	3.1		0.81		once pyrolyzed	

distillation, using an efficient column (meta and para), or by vacuum distillation (ortho). Successive pyrolysis showed that in the case of metaand para-fluorotoluenes these products were sufficiently pure for our purpose, while in the case of the ortho-compound a constant rate of decomposition was reached after the first pyrolysis.

The results of the pyrolysis of toluene and of the three fluoro-toluenes are summarized in Table I. In the last column are the ratios of the observed k_u to the average value of the k_u for toluene. The deviations of these ratios from their mean value indicate the magnitude of the experimental errors involved in these measurements. The following points should be emphasized:

(a) No C_2 hydrocarbons nor any HF were observed in the products of the pyrolysis.***

(b) The crystalline products of the pyrolysis of the fluoro-toluenes were isolated and identified as the corresponding di-fluoro-dibenzyls.⁶ The quantities in which these compounds are formed during the pyrolysis indicate, as was expected if we apply here the reaction mechanism suggested for the pyrolysis of toluene, that their production corresponds to the stoichiometric proportion of one mole of dibenzyl derivative for one mole of H_2 or CH_4 produced.

(c) The analysis, recorded in Table II, of the gas

TABLE Ib.

				Extrapolated	to T = 1120°K	
		%	ku ·103	k1120 ·103 sec1	k1120	
Run	T⁰K	Decomp	. sec1		Average k toluene	Remarks
Tolue	ene					
31	1117	0.390	16.0	17.2)	0.90	
32	1117	0.367	15.9	17.1	0.90	
33	1118	0.379	16.3	16.8 average	0.89	
46	1132	0.705	29.6	20.1 for	1.05	
47	1120	0.437	18.6	18.0 (1120°K	0.94	
51	1130	0.695	31.3	22.6 19.1	1.18	
52	1124	0.550	25.2	21.7	1.13	
53	1118	0.419	18.7	19.6	1.02	
Para-	fluoro-t	oluene				
34	1108	0.324	12.1	17.5	0.92)	twice pyrolyzed
36	1124	0.495	18.2	15.7	0.80	twice pyrolyzed
37	1123	0.565	21.8	17.4	0.92 average	twice pyrolyzed
38	1119	0.495	18.9	18.9	0.99 (0.920	twice pyrolyzed
44	1124	0.616	21.9	18.8	0.98	three times
Meta	-fluoro-	toluene			,	F J ,
39	1121	0.465	17.8	16.8	0.88)	not pyrolyzed
40	1122	0.430	16.2	14.8	0.78 average	not pyrolyzed
41	1117	0.342	13.5	14.5	0.76 0.805	once pyrolyzed
42	1121	0.455	16.3	15.4	0.80	once pyrolyzed

TABLE IC.

	Extrapolated to $T = 1090$ °K								
		07	$k_{11} \cdot 10^{3}$		k 1090				
Run	Т°К	Decomp.	sec1	$k_{1090} \cdot 10^3 \text{ sec.}^{-1}$	average k toluene	Remarks			
Tolue	ne	••••							
70	1090	0.18	8.0	7.75) average	0.99				
71	1091	0.19	8.6	8.02 for	1.02				
72	1091	0.18	8.3	7.74 1090°K	0.98				
Ortho	-fluoro	-toluene		1.04 (
74	1090	0.22	7.25	7.2	0.92	once pyrolyzed			
75	1093	0.21	7.7	6.9	0.88	once pyrolyzed			
76	1091	0.22	7.1	6.8	0.87 Laverage	twice pyrolyzed			
77	1092	0.19	6.4	5.9	0.76 0.860	twice pyrolyzed			
95	1089	0.19	6.6	6.9	0.88	three times pyrolyzed			

produced in the pyrolysis shows that the H_2/CH_4 ratio for the para- and meta-fluoro-toluene is the same as for toluene,¹ while the gas produced in the pyrolysis of orthofluoro-toluene has a composition similar to that observed for ortho-xylene.¹

(d) The rates of pyrolysis of all three fluoro-toluenes lie within a range 20 percent of the rate of pyrolysis of toluene at the same temperature.

In view of these results we have no hesitation in regarding the decomposition of the fluorotoluenes as based on the same mechanism as that suggested for toluene.

DISCUSSION

The present results show that the C-H bond energy in all three fluoro-toluenes is nearly the same as the C-H bond energy in toluene, i.e., about 78 kcal./mole. If we assume the entropy of activation in the decomposition of all these compounds to be exactly the same, the small decreases in the k_u of the fluoro-toluenes, as compared with that of toluene, lead to changes

^{***} In a few cases the pyrolysis of ortho-fluoro-toluene produced products recorded as C_2 hydrocarbon. These results, however, were rare and probably due to traces of water.

⁶ These compounds are not described yet in the literature. Our note describing their identification and properties will be sent elsewhere.

in the C-H bond energy of $\pm 0.2-0.4$ kcal./mole only (experimental error is ± 0.2 kcal./mole). Calculations based on electrostatic interaction between the C-F and the C-H dipoles show that the energy lost by the breaking of the C-H bond is of the order 0.04-0.25 kcal./mole. The observed variations in k_u (10 percent for parafluoro-toluene, 20 percent for meta-fluoro-toluene, and 15 percent for ortho-fluoro-toluene) could be amply explained as a result of these dipole interactions, as also by the small variations in the entropy of activation, which is obviously not exactly constant.

At any rate, the influence of the dipole interaction on the bond energy is very small, amounting to a mere fraction of a kcal./mole. The last conclusion is important for the problem of the C-H bond energy in para-xylene. It was reported by Szwarc¹ that the C-H bond energy in para-xylene is less by 2.5 kcal. than the C-Hbond energy in toluene, and the observed decrease in the C-H bond energy was explained by hyperconjugation. There had been the possibility, however, to ascribe the decrease of bond energy to the effect of electrostatic interaction between the two CH_3 groups. This possibility is now ruled out and the presence of hyperconjugation definitely established.

THE INFLUENCE OF THE DIPOLE IN IONIC REACTIONS

The apparent absence of any influence of the field effect of the bond energy is in contrast to the well-known fact that dipoles affect strongly the equilibria and reaction rate in ionic reactions. The difference is due to the fact that the energy of the electrostatic interaction between a dipole

TABLE II. Gas analysis.

Compound	%H2	%Сн
l'oluene	60%	40%
Para-fluoro-toluene	{59% 61%	{41% 39%
Meta-fluoro-toluene	59%	41%
	(41%)	59%
Ortho-fluoro-toluene	47%	53% 54%

and an electric charge is much greater than the energy of interaction between two dipoles. Using, for example, the previous method of calculation, we find that the replacement of the C-H dipole in para-fluoro-toluene by a oneelectron charge in the *p*-fluoro-benzyl ion increases the energy of the electrostatic interaction about one hundred times. All the regularities which are summarized in Hammett's σ -factors are due not to the interactions between dipoles but to the much greater interactions between dipoles and electric charges of the ions produced in the final states (affecting equilibria), or in the transition states (affecting rates of reaction).

The same conditions prevail in aromatic substitution reactions. Substitutions caused by ionic reagents are governed by the charge distribution in the molecule, which is strongly influenced by the dipole action. On the other hand, substitution caused by radical reagents does not show any dipole effect, as is well known in the chemistry of free radicals.

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