Table I

Radicals Observed in Ultraviolet Irradiated Methanol at 77°K.

Radical	Lines	Observed line width (gauss)	Observed hyperfine splitting (gauss)
$\cdot CH_2OH$	Triplet	11	18
$\cdot CH_2OD$	Triplet	7–8	17
$\cdot CH_3$	Quartet	3–4	23.5
$\cdot CHO$	Doublet	8–10	130
$\cdot CDO$	Triplet	5–6	19.5
$\cdot CD_3$	Septet	1.7	3.5
$\cdot CD_2OH$	Quintet	1–2	3–4
$\cdot COD$	Singlet	3–4	. . .
$\cdot COH$	Singlet	4–5	. . .
$CH_3O\cdot$	Singlet	45	. . .
$CD_3O\cdot$	Singlet	18	. . .

The radicals above the line are those identified with considerable certainty, whereas the ones listed below the line are identified with somewhat less certainty. It will be noted that $\cdot CH_2OH$ gives a triplet of about the same hyperfine splitting as $\cdot CH_2OD$, but the line width is less in the latter case, indicating some influence of the hydroxyl hydrogen or deuterium. Such narrowings of lines can come about if deuterium is present in the crystal but not bound in the radical itself. These effects have been discussed previously by Zeldes and Livingston.[3]

In conclusion, some comments should be made about relative stabilities for the radicals observed in this investigation. In general it was found that oxygen-containing radicals had considerably longer lifetimes than non-oxygenated radicals such as $\cdot CH_3$. The formyl radical and $\cdot CH_2OH$ can be produced at 90°K., whereas $\cdot CH_3$ did not even appear under our conditions. The oxygen-containing radicals could be kept indefinitely at 77° K.; however, $\cdot CH_3$ decayed within 2 hr. under such conditions. The $\cdot CH_3$ radical apparently can tumble rapidly as evidenced from its sharp line symmetrical spectrum. The motion of $\cdot CHO$ exhibited considerable hindrance as indicated by its asymmetric spectrum. These differences probably arise because of the hydrogen bonding in the case of oxygen-containing radicals.

There is also a good indication that the deuteriated radical $\cdot CD_3$ is more stable than $\cdot CH_3$. For example, $\cdot CD_3$ in methanol was kept for 4 days at 77°K. without any pronounced change in its seven line spectrum; and gradual warmup did not weaken the spectrum appreciably until the temperature rose above 95°K.

Acknowledgment.—We wish to thank Dr. Jack A. Simmons for his valuable suggestions during our many discussions.

[Contribution from the Department of Chemistry, University of Toronto, Toronto 5, Canada]

The Structure of Substituted C_7 Ions from Benzyl Derivatives at the Appearance Potential Threshold

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The appearance potentials of ions of the general formula $RC_7H_6^+$ have been measured from a number of *meta* and *para* substituted benzyl derivatives $RC_6H_4CH_2X$. The combinations studied were R = CH_3 (X = H and Br), R = F (X = H and Br), R = OH (X = H and CH_3) and R = CH_3O (X = Cl). From a comparison of the effect of substitution in the *meta* and *para* position it is suggested that when R is CH_3, F, or OH the ion formed at the threshold has the symmetrical tropylium structure, but that when R is CH_3O the ion at the threshold has the benzyl structure. The heats of formation of the $CH_3C_7H_6^+$ and $FC_7H_6^+$ ions are estimated and compared with heats of formation calculated for the isomeric substituted benzyl ions. The appearance potentials of $RC_6H_4O^+$ ions from *meta* and *para* substituted anisoles have been shown to follow a linear relation with the σ^+ values for the substituents.

Introduction

Considerable evidence has been presented[1–4] indicating that the $C_7H_7^+$ ion found in abundance in the mass spectra of toluene and other benzyl derivatives is the symmetrical tropylium ion rather than the benzyl ion. This evidence has been obtained chiefly through carbon-13 and deuterium labelling and is based on the observation that the ring and side-group carbon and hydrogen atoms become indistinguishable in the $C_7H_7^+$ ion. This conclusion is based on the distribution of the label in the $C_5H_5^+$ ion which is formed from the $C_7H_7^+$ ion by the process

$$C_7H_7^+ \longrightarrow C_5H_5^+ + C_2H_2$$

These results refer therefore to $C_7H_7^+$ ions which have sufficient energy to undergo further decomposition and do not provide information of the structure of the $C_7H_7^+$ ion at the appearance potential threshold. Furthermore, recent electron impact work[5] on tropylium derivatives has led to the conclusion that the heat of formation of the tropylium and benzyl ions are the same within experimental error, with the consequence that the structure of the $C_7H_7^+$ ion at the appearance potential threshold cannot be established on the basis of the heat of formation of the ion.

The mass spectra of ring-substituted benzyl derivatives $RC_6H_4CH_2X$ frequently show large peaks for the ion $RC_7H_6^+$ analogous to the $C_7H_7^+$ ion in benzyl compounds. The present work reports the

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(1) P. N. Rylander, S. Meyerson and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957).

(2) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).

(3) S. Meyerson and P. N. Rylander, *J. Phys. Chem.*, **62**, 2 (1958).

(4) S. Meyerson, P. N. Rylander, E. L. Eliel and J. D. McCollum, *J. Am. Chem. Soc.*, **81**, 2606 (1959).

(5) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *ibid.*, **82**, 5593 (1960).

appearance potentials of a number of these substituted C_7 ions and presents evidence, based on the effect of the substituents, concerning the structure of the ions at the appearance potential threshold.

Recently,[6] the ionization potentials of a number of *meta* and *para* substituted benzyl radicals have been measured by electron impact. Since the bond dissociation energies of ring-substituted benzyl derivatives appear to be essentially independent of the nature of the substituent,[7] these ionization potentials are, in fact, a measure of the effect of the substituents on the energy required for benzyl ion formation from the neutral molecule in the gas phase. It was observed that a number of substituents showed large differences in the stabilization of the benzyl ion dependent on whether the substituent was in the *meta* position or in the *para* position capable of conjugating with the positive charge. This result suggested that substituent effects might be useful in determining the structure of the substituted C_7 ion formed in the dissociative ionization and prompted the present investigation.

If, in the dissociative ionization, the ion $RC_7H_6^+$ has the benzyl structure at the threshold with the ring orientation of the substituent maintained, one would expect the *meta* and *para* isomers to differ in appearance potentials by the same amount as was found for the respective benzyl radicals. On the other hand, if rearrangement to the symmetrical tropylium structure has occurred at the appearance potential threshold, the *meta–para* orientation will have lost its significance. In this case one would expect the appearance potentials of the $RC_7H_6^+$ ion from the two ring isomers to be identical. As will be seen in the following both types of behavior have been encountered.

Experimental

The appearance potentials were determined using an Associated Electrical Industries MS-2 mass spectrometer. This instrument is of the 90° sector type with a six-inch radius of curvature and employs magnetic scanning. The ionizing electron current was regulated at 20 μamp. with the case and trap held at the same voltage. The electron voltage could be read to ± 0.02 v. either by a meter supplied with the mass spectrometer or by a precision voltmeter added to the instrument. The voltage scale was calibrated by use of a rare gas, usually xenon, admitted with the sample.

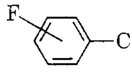
The ionization efficiency curves for the unknown and standard gas were determined as a function of electron energy in 0.2 v. steps over the voltage range giving ion currents of 10% of the 50 v. value to the lower limit of detection, which was usually less than 0.1% of the 50 v. peak. The 50 v. peaks were adjusted to the same height by variation of the pressure and normally corresponded to an ion current of 2 to 4 × 10^{-11} amp. As is usually found for fragment ions, the ionization efficiency curves for the standard and unknown were not parallel when plotted in the semi-logarithmic manner.[8] The threshold voltage was evaluated by extrapolation of the voltage difference between the two curves to zero ion current.

For the C_7 ions from the benzyl derivatives the results obtained in this fashion showed that the appearance potentials from the isomeric molecules were identical within experimental error, with the exception of the methoxy derivatives. However, due to the curvature of the voltage difference extrapolation, this experimental error was rather large (0.1 v.).

It was observed that when the ionization efficiency curves for $RC_7H_6^+$ from the two isomers were obtained under identical conditions, the curves for the standard gas were superimposable when plotted in the semi-logarithmic manner. This permitted a direct comparison of the semi-log plots for the $RC_7H_6^+$ ion from the two isomers. It was found that these curves were normally parallel as well and consequently the extrapolation of the voltage difference between these two curves showed little curvature. This reduced the errors inherent in the extrapolation procedure with the consequence that the appearance potential differences could be obtained with greater accuracy. It should be emphasized that this procedure does not offer any advantages if the ionization efficiency curves are not similar in form. To test the reproducibility of this method of evaluating the appearance potential differences, several determinations were made for the $FC_7H_6^+$ ion from the isomeric fluorotoluenes. The results, summarized in Table I, lead to the conclusion that the appearance potential difference can be evaluated by this method to at least ±0.05 v. The appearance potential differences recorded in Table III were evaluated by this method. The absolute appearance potentials recorded in Tables II and V were evaluated by the extrapolation of the voltage difference between standard and unknown to zero ion current and consequently have larger limits of error.

TABLE I

REPRODUCIBILITY OF APPEARANCE POTENTIAL DIFFERENCE MEASUREMENT



$$+ \; e \longrightarrow FC_7H_6^+ + H + 2e$$

Determination	*A* (*meta*) − *A* (*para*)
1	+0.02
2	− .03
3	+ .03
4	+ .03
5	+ .01
Average	±0.01 ± 0.02

TABLE II

APPEARANCE POTENTIALS OF $RC_6H_4O^+$ IONS FROM SUBSTITUTED ANISOLES

R	Appearance potential (volts ± 0.1)
p-CN	12.68
m-OH	11.92
p-Br	11.78
H	11.86
m-MeO	11.57
p-F	11.53
m-Me	11.33
p-Me	10.83
p-OH	11.01
p-MeO	10.37
p-NH_2	9.67

TABLE III

APPEARANCE POTENTIAL DIFFERENCES FOR *meta* AND *para* SUBSTITUTION

R	X	Experimental *A* (*meta*) − *A* (*para*)	Theoretical[a] *A* (*meta*) − *A* (*para*)
CH_3	H	−0.02 ± 0.05	0.28 (0.19)
CH_3	Br	.01 ± .05	.28 (.19)
F	H	.01 ± .05	.50 (.40)
F	Br	.07 ± .05	.50 (.40)
HO	H	− .08 ± .05	.66
HO	CH_3	− .03 ± .05	.66
CH_3O	Cl	1.15 ± .1	.99

[a] Calculated on the basis of benzyl ion formation.

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(6) A. G. Harrison, P. Kebarle and F. P. Lossing, *ibid.*, **83**, 777 (1961).

(7) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths, London, 1958.

(8) F. P. Lossing, A. W. Tickner and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

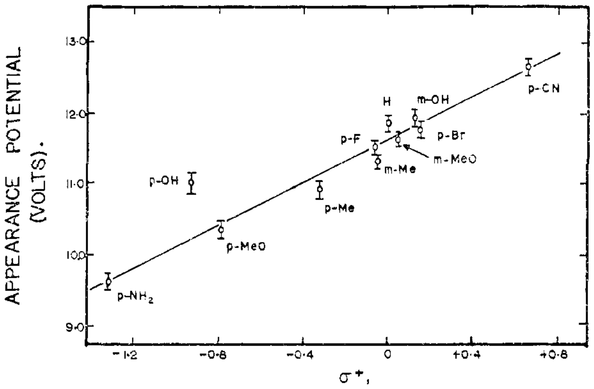

Fig. 1.—Appearance potentials of $RC_6H_4O^+$ ions plotted against σ^+.

It was found that the repeller voltage had some effect on the measured appearance potentials although not on the differences. Determination 4 in Table I was carried out with 1 v. repeller, the remainder being carried out with case and repeller at the same voltage. With 1 v. repeller the measured appearance potentials were 0.3 v. higher than the average of the other determinations, although the difference in appearance potentials from the two isomers was not affected. A similar effect of repeller voltage has been observed for loss of hydrogen in the alkanes.[9] The appearance potentials reported in the following were obtained with zero repeller voltage.

Materials.—With the exception of the *m*-methoxybenzyl chloride and the fluorobenzyl bromides all compounds were commercial samples of high purity. The preparation of the fluorobenzyl bromides has been described previously.[8] The *m*-methoxybenzyl chloride was prepared from *m*-methoxybenzoic acid through reduction of the methyl ester to the alcohol with $LiAlH_4$[10] and conversion of the alcohol to the chloride by reaction with phosphorus trichloride.[11] The chloride was purified by vacuum distillation, the fraction boiling at 102–103° (9 mm.) being retained (lit.[12] 106–108° 12–14 mm.).

Results and Discussion

Before discussing the results for the substituted C_7 ions it is necessary to consider two assumptions upon which rests the interpretation of the results. The first assumption is that in the dissociative ionization of benzene derivatives the orientation of the substituents will normally be maintained if the central skeletal structure of the ion is maintained. The effect of substituents on the energy of benzyl ion formation was obtained from the study of the ionization potentials of benzyl radicals.[6] This is a simple ionization process, usually considered to occur by a vertical transition, with the result that there is no opportunity for rearrangement. However, in the initial excited ion formed in a dissociative ionization the possibility exists that the substituent becomes mobile, with the consequence that orientation effects will not be observed. Second, the interpretation of the results rests, in part, on the assumption that the effect of the methoxy and hydroxy substituents on the energy of benzyl ion formation can be predicted from the correlation of this energy with the σ^+ values for the substituents. Such a correlation has been shown[6] for a number of substituents, including *p*-methoxy, but the *m*-methoxy and the hydroxy groups were not studied.

To offer some support for these assumptions the energetics of the dissociative ionization

$$RC_6H_4OCH_3 + e \longrightarrow RC_6H_4O^+ + CH_3 + 2e$$

where R may be in either the *meta* or *para* position, was studied. The results are recorded in Table II and shown graphically in Fig. 1 plotted against the σ^+ values for the substituents.[13]

With the exception of the para hydroxy group the correlation with σ^+ is satisfactory. A similar deviation for this group has been found in the correlation of ionization potentials of substituted benzenes and toluenes with σ^+ values.[14] The results in Fig. 1, in agreement with the results of Crable and Kearns, suggest that a σ^+ value of -0.4 for *p*-OH is more appropriate than the original value of -0.92, when considering gas phase ionization reactions. It is interesting to note that the graph in Fig. 1 has a slope very close to that for the similar correlation of the energy of benzyl ion formation.[6]

The results of Fig. 1 offer further evidence that the σ^+ values derived from solution kinetics can be used to correlate the gas phase ionization of benzene derivatives and make it appear plausible to deduce the effect of hydroxy and methoxy substitution on the energy of benzyl ion formation from such a correlation. The results also show that in this case the orientation of substituents is maintained in the dissociative ionization and that mobility of the substituent groups is not necessarily encountered.

Table III records the differences in appearance potentials from the *meta* and *para* isomers for the dissociative ionization

$$RC_6H_4CH_2X + e \longrightarrow RC_7H_6^+ + X + 2e$$

Columns 1 and 2 of the table indicate the combinations of R and X studied. Column 3 records the differences in appearance potentials, *A*(*meta*)—*A*(*para*), determined as previously outlined, while column 4 records the appearance potential differences one would expect if the ions formed at the threshold were the respective benzyl ions. Since the bond dissociation energies of benzyl derivatives are independent of substituent,[7] this value can be estimated directly from the differences in ionization potentials of the benzyl radicals for the fluoro and methyl substituents. The necessary ionization potentials have not been measured for some of the other cases; however, as previously mentioned the energy of benzyl ion formation has been shown to follow a linear relation when plotted against the σ^+ values for the substituents. Therefore the *A*(*meta*)−*A*(*para*) values recorded in column 4 were estimated from this correlation using $\sigma^+ = -0.4$ for the *p*-OH group (see above) and σ^+ values for the other substituents given by Brown and Okamoto.[13] The values in parentheses for the methyl and fluoro substituents have been estimated directly from the ionization potentials of the radicals.

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(9) L. Friedman, F. A. Long and M. Wolfsberg, *J. Chem. Phys.*, **31**, 755 (1959).

(10) W. G. Brown in "Organic Reactions," Vol. VI, J. Wiley and Sons, New York, N. Y., 1951, p. 469.

(11) R. Pschorr, *Ann.*, **391**, 44 (1912).

(12) K. U. Leushina and S. I. Sergievskaya, *Zhur. Obshchei Khim.*, **24**, 905 (1954) (*Chem. Abstr.*, **49**, 12328e (1955)).

(13) H. G. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958). This reference does not give a σ^+ value for *m*-OH. The σ value was therefore used and as shown gives a satisfactory correlation.

(14) G. F. Crable and G. L. Kearns, paper presented at A.S.T.M. Committee E-14 Meeting, Chicago, June, 1961.

The agreement between the two methods is satisfactory.

The results in Table III show that, with the exception of the methoxy derivatives, in each case the appearance potentials of the $RC_7H_6^+$ ion from the *meta* and *para* isomers are identical within experimental error. This result is in distinct contrast with the predictions in column 4, made on the basis of the benzyl ion structure, and also in contrast with the effect of substituents on the energy of ion formation in the anisoles (Fig. 1). The interpretation of the results when hydrogen is the neutral fragment in the dissociative process is uncertain. Labelling experiments[1] have shown that for the $C_7H_7^+$ ion from toluene the hydrogen lost does not come exclusively from the side-chain methyl. Undoubtedly the same is true in the present case; in addition it will be shown below that excess energy is involved in these processes. The results show only that stabilizing effects due to substituent orientation have been lost in the ion formed at the threshold.

When the neutral fragment in the dissociative ionization is chlorine, bromine or methyl the situation is somewhat clearer and structural considerations would suggest that the simplest process would form the respective benzyl ions. However, if the benzyl type ions were formed at the threshold with the orientation of the substituents maintained one would expect the appearance potentials to reflect the differences given in column 4. In the case of the methoxybenzyl chlorides such a difference is found experimentally indicating that the ions formed have the benzyl structure with the *meta-para* orientation of the methoxy group maintained. For the $FC_7H_6^+$ ion from the fluorobenzyl bromides, the $CH_3C_7H_6^+$ ion from the xylyl bromides, and the $HOC_7H_6^+$ ion from the ethylphenols the relative stabilizing effects due to substituent orientation are not reflected in the measured appearance potential differences. Such effects are found for the methyl and fluoro cases in the ionization of the benzyl radicals and for the methyl and hydroxy groups in the formation of the $RC_6H_4O^+$ ion. One must conclude that the *meta–para* orientation of the substituents has been lost in the ion formed at the threshold. This might be taken to indicate that in these cases the substituent is capable of migrating freely in the ring with the carbon skeleton retaining the benzyl structure. That this is not a general occurrence is shown by the results for the methoxy substituents and by the results in Fig. 1. Alternatively the results can be explained simply by assuming that the carbon skeleton rearranges to the symmetrical tropylium structure at the threshold, since in this ion *meta–para* orientation has no significance. In view of the strong evidence for the tropylium ion at higher energies, it is suggested that the tropylium structure for the ion at the threshold is more probable. By analogy one would expect the ions formed by loss of hydrogen to have the same structure.

The *meta* and *para* methoxybenzyl chlorides appear to give the respective benzyl ions at the appearance potential threshold. There is no doubt that the orientation of the substituents is maintained, the measured appearance potential difference being in satisfactory agreement with that predicted on the basis of benzyl ion structure. The mass spectra of the isomeric methoxy derivatives show rather large differences which are not found in the mass spectra of other isomeric benzyl derivatives. Partial mass spectra for the two isomers are given in Table IV. The spectra are consistent with the fact that the $m/e = 121$ ion from the *meta* isomer is a much higher energy ion than that from the *para* isomer. Thus for the *meta* isomer the abundance of this ion relative to the fragment ion, $m/e = 91$, or the parent ion is much less than for the *para* isomer. Not only is more energy required for formation of this ion, but the endothermicity for the further decomposition of the ion is considerably less. It is interesting to note that the mass spectra, in addition to the significant peak at $m/e = 91$, also show a metastable at $m/e = 68.4$, corresponding to the transition

$$CH_3OC_6H_4CH_2^+ \longrightarrow C_7H_7^+ + CH_2O$$

It would appear that when the ring expands loss of formaldehyde occurs with formation of the tropylium ion rather than the methoxy-substituted tropylium ion.

TABLE IV

PARTIAL MASS SPECTRA OF METHOXYBENZYL CHLORIDE

m/e	Formula	Peak height *meta*	Peak height *para*
156	$CH_3OC_6H_4CH_2{}^{35}Cl^+$	32.0	13.0
121	$CH_3OC_6H_4CH_2^+$	100.0	100.0
91	$C_7H_7^+$	31.9	9.3
65	$C_5H_5^+$	7.9	3.3

TABLE V

APPEARANCE POTENTIALS AND IONIC HEATS OF FORMATION

R	X	Appearance potentials (± 0.1 v.) *meta*	*para*	ΔH_f-($RC_6H_4CH_2X$) kcal./mole	ΔH_f-($RC_7H_6^+$) kcal./mole
CH_3	H	11.84	11.86	4.2	225
CH_3	Br	9.44	9.44	11	202
F	H	11.92	11.89	−34	188
F	Br	9.85	9.93	−27	174
HO	H	12.33	12.41		
HO	CH_3	10.80	10.83		
CH_3O	Cl	9.85	8.69		

The experimental values for the measured appearance potentials are listed in Table V. As previously discussed the limits of error assigned to these values are considerably larger than those assigned to the appearance potential differences, due to the nature of the extrapolation. Also recorded in Table V are the heats of formation for the $CH_3C_7H_6^+$ and $FC_7H_6^+$ ions calculated from the measured appearance potentials by the relationship

$$A = \Delta H_f(RC_7H_6^+) + \Delta H_f(X) - \Delta H_f(RC_6H_4CH_2X)$$

using $\Delta H_f(H) = 52.1$ kcal./mole,[15] $\Delta H_f(Br) = 27$ kcal./mole[15] and the $\Delta H_f(RC_6H_4CH_2X)$ values given in column 5. The heat of formation of xylene listed is the average of ΔH_f(*m*-xylene) = 4.1 kcal./mole and ΔH_f (*p*-xylene) = 4.3 kcal./mole.[16]

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(15) F. D. Rossini, *et al.*, National Bureau of Standards Circular No. 500 (1952).

(16) F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.

The remaining values have been estimated as discussed below and must be considered as approximate values.

The heat of formation calculated for the CH_3-$C_7H_6^+$ ion from the xylyl bromides is practically identical with the values ΔH_f(*m*-xylyl$^+$) = 203 kcal./mole and ΔH_f(*p*-xylyl$^+$) = 200 kcal./mole calculated from the measured ionization potentials of the xylyl radicals,[17] I(*m*-xylyl) = 7.65 v., I (*p*-xylyl) = 7.45 v. and the kinetically determined bond dissociation energies,[7] D(xylyl–H) = 77 kcal./mole using the relation

$$\Delta H_f(CH_3C_6H_4CH_2^+) = I(CH_3C_6H_4CH_2) + D(CH_3C_6H_4CH_2{-}H) - H_f(H) + \Delta H_f(CH_3C_6H_4CH_3)$$

It is clear that the structure of the ion cannot be elucidated from a consideration of ionic heats of formation. Since, as discussed previously, the *meta*–*para* orientation of the methyl group is lost in the dissociative process, it is felt that the heat of formation calculated from the appearance potential data probably refers to the substituted tropylium ion. It would therefore appear that the heats of formation of the isomeric substituted benzyl ion and tropylium ion are the same within experimental error. This conclusion is similar to that derived for the benzyl–tropylium case where the isomeric ions have similar heats of formation.[5]

The heat of formation of the $CH_3C_7H_6^+$ (or $C_8H_9^+$) ion formed from the xylenes is identical with the average value $\Delta H_f(C_8H_9^+)$ = 224 kcal./mole obtained by Field and Franklin[18] from a study of the processes

$$1,3\text{-}C_6H_4(CH_3)(n\text{-}C_3H_7) + e \longrightarrow C_8H_9^+ + C_2H_5 + 2e,\ A = 11.16 \pm 0.10$$

$$1,4\text{-}C_6H_4(CH_3)(n\text{-}C_3H_7) + e \longrightarrow C_8H_9^+ + C_2H_5 + 2e,\ A = 10.97 \pm 0.10$$

Field and Franklin also measured the appearance potentials of the $C_8H_9^+$ ion from the isomeric 1,3-diethyl- and 1,4-diethylbenzenes. The $C_8H_9^+$ ion formed by loss of an ethyl radical was found to have a heat of formation of 224 kcal./mole. They concluded that the ion did not have the expected phenyl structure but had rearranged to the benzyl structure. It would appear more probable that rearrangement to the tropylium structure has occurred and that the ion has been formed with excess energy.

The heats of formation ΔH_f(*p*-$FC_6H_4CH_2^+$) = 171 kcal./mole and ΔH_f(*m*-$FC_6H_4CH_2^+$) = 180 kcal./mole may be calculated from I(*p*-$FC_6H_4CH_2$) = 7.78 v.[6], I(*m*-$FC_6H_4CH_2$) = 8.18 v.[6] and D-($FC_6H_4CH_2$—H) = 78 kcal./mole.[7] The heat of formation of the $FC_7H_6^+$ ion from the fluorobenzyl bromides is very close to these values, while the ion from the fluorotoluenes has a heat of formation about 14 kcal./mole greater. Again, the evidence from the effect of substituents suggests that the ion formed in the dissociative process has the tropylium structure and it would appear that the isomeric benzyl and tropylium ions have similar heats of formation.

Estimation of Heats of Formation.—The heats of formation of benzene, toluene and xylene (average of *meta* and *para* isomers) are, respectively, 19.8, 12.0 and 4.2 kcal./mole,[16] showing an increment of 7.8 kcal./mole for replacement of a ring-hydrogen by a methyl group. Combining this increment with $\Delta H_f(FC_6H_5)$ = −26.5 kcal./mole[19] gives $\Delta H_f(FC_6H_4CH_3)$ = −34 kcal./mole, approximately.

From ΔH_f(toluene) = 12.0, ΔH_f(benzyl bromide) = 18.4 kcal./mole,[20] ΔHf(propylene) = 4.9 kcal./mole[16] and ΔH_f(allyl bromide) = 12.1 kcal./mole,[21] the average increment for replacement of an allylic hydrogen by bromine is 6.8 kcal./mole. Combining this with the heats of formation of xylene and fluorotoluene gives the approximate values, ΔH_f(xylyl bromide) = 11 kcal./mole and $\Delta H_f(FC_6H_4CH_2Br)$ = −27 kcal./mole.

Acknowledgment.—The authors are grateful to the National Research Council of Canada for financial support of this work.

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[17] J. B. Farmer, F. P. Lossing, D. G. H. Marsden and C. A. McDowell, *J. Chem. Phys.*, **24**, 52 (1956).

[18] F. H. Field and J. L. Franklin, *ibid.*, **22**, 1895 (1954).

[19] D. W. Scott, *et al.*, *J. Am. Chem. Soc.*, **78**, 5457 (1956).

[20] S. W. Benson and J. H. Buss, *J. Phys. Chem.*, **61**, 104 (1957).

[21] O. H. Gellner and H. A. Skinner, *J. Chem. Soc.*, 1145 (1949).