The Energy of the Methyl Group-Triple Bond Hyperconjugation

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It has been qualitatively shown previously that the difference in the rates of decarboxylation of sodium tetrolate and sodium propiolate is mainly determined by hyperconjugation. In the present paper a quantitative study of the phenomenon is presented which is based on the assumption that under ideal conditions the difference in the activation energies for the decarboxylation of these compounds is equal to the experimentally determined energy of hyperconjugation between a methyl group and the triple bond. By determining the rates of decomposition of the above salts under conditions where solvation is a minimum, a limiting value, $3\,440 \pm 200$ cal., has been calculated for the activation energy difference. By adding 1 100 cal. to this value as proposed by R. S. Mulliken, the value of the theoretical energy of hyperconjugation comes out to 4 540 cal., which is practically the same as the value computed by R. S. Mulliken and coworkers for the energy of hyperconjugation in methylacetylene by the molecular orbital method.

In a previous work¹ it was concluded the difference in the rates of decomposition of sodium propiolate and sodium tetrolate is primarily due to hyperconjugation in the latter compound. In the present study, this conclusion is considered on the basis of additional kinetic data.

EXPERIMENTAL

Materials. The propiolic, tetrol and *tert.* butylpropiolic acids employed were those used in the previous studies^{1,2}. The sodium salts of these acids were prepared as described earlier². Dioxan (Merck) was purified by the method of Hess and Frahm³, after which its melting point was 11.8° C. Ethanol (absolute ethanol, Oy Alkoholiliiike, Rajamäki) was dried with aluminium using HgCl_2 as activator. Benzene (Merck, benzene free from thiophene) was refluxed over sodium wire and then distilled. The water was ordinary distilled water.

Measurements. The kinetic measurements were performed as described previously² using the same calibrated apparatus.

RESULTS

The decomposition of sodium propiolate was studied in an ethanol-dioxan mixture, that of sodium tetrolate in absolute ethanol, in two ethanol-benzene mixtures and in a dioxan-water mixture, and the decomposition of sodium *tert.* butylpropiolate in a dioxan-water mixture. In all experiments the initial concentration of the salt was 0.02 *M*. In the case of the above solvent mixtures, an attempt was made to increase the proportion of the non-polar component as far as possible without exceeding the precipitation limit of the salt at room temperature. This did not succeed for sodium tetrolate and sodium *tert.* butylpropiolate in the case of the dioxan-water mixtures, since these salts give 0.02 *M* solutions even in the 95 % dioxan-water mixture, which latter mixture, however, appeared to be unstable at the temperatures at which the experiments were performed. For this reason, sodium tetrolate was studied only in the approximately 80 % dioxan-water mixture and sodium *tert.* butylpropiolate in the approximately 60 % dioxan-water mixture. All the reactions were conducted in a nitrogen atmosphere.

The decompositions followed the first-order law in all solvents studied and the maximum deviations of the $\log k - 1/T$ points from the Arrhenius plots did not exceed 1 % except for sodium *tert.* butylpropiolate, for which the maximum deviation was approximately 2 %. The calculations were carried out using the same equations as previously².

The rate constants are given in Table 1 and the values of the derived kinetic quantities in Table 2. The activation energies E and frequency factors A have been calculated by the method of least squares. The values of the free energy of activation ΔG^* , heat of activation ΔH^* and the entropy of activation ΔS^* refer to 100° C.

Table 1. Specific reaction rates for sodium propiolate, sodium tetrolate and sodium *tert.* butylpropiolate in various solvent mixtures.

Reactant	Solvent composition in wt %		10 ⁴ <i>k</i> sec. ⁻¹				
			73.85°	82.32°	90.64°	98.92°	106.78°
HC≡C—COONa	Dioxan, 28.77% + EtOH		3.71	9.27	25.9	69.1	167
		106.78°	114.88°	122.39°	130.19°	137.33°	144.32°
CH ₃ —C≡C—COONa	Dioxan, 80.59% + H ₂ O			29.1	69.2	150	302
CH ₃ —C≡C—COONa	Ethanol	5.38	*	33.0	**	160	
CH ₃ —C≡C—COONa	Benzene, 52.59 % + EtOH	4.90		30.9		156	
CH ₃ —C≡C—COONa	Benzene, 58.90 % + EtOH	4.84	12.8	30.8	73.0	157	
				122.39°	130.19°	137.23°	144.32°
(CH ₃) ₃ C—C≡C—COONa	Dioxan, 61.32 % + H ₂ O			19.1	42.0	87.1	178

* 115.03°: 14.2.

** 130.14°: 76.9.

Table 2. Derived kinetic quantities for the decomposition of sodium propiolate, sodium tetrolate and sodium tert. butylpropiolate in various solvent mixtures.

Reactant	Solvent composition in wt %	$A \text{ sec.}^{-1}$	$E \text{ cal.}$	$\Delta G^* \text{ cal.}$	$\Delta H^* \text{ cal.}$	$\Delta S^* \text{ E.U.}$
$\text{HC}\equiv\text{C}-\text{COONa}$	Dioxan, 28.77 % + EtOH	$3.59 \cdot 10^{14}$	31 860	29 030	31 130	+ 5.6
$\text{CH}_3-\text{C}\equiv\text{C}-\text{COONa}$	Dioxan, 80.59 % + H_2O	$7.06 \cdot 10^{14}$	35 080	31 740	34 340	+ 7.0
$\text{CH}_3-\text{C}\equiv\text{C}-\text{COONa}$	Ethanol	$3.57 \cdot 10^{14}$	34 460	31 620	33 710	+ 5.6
$\text{CH}_3-\text{C}\equiv\text{C}-\text{COONa}$	Benzene, 52.59 % + EtOH	$7.59 \cdot 10^{14}$	35 100	31 700	34 360	+ 7.1
$\text{CH}_3-\text{C}\equiv\text{C}-\text{COONa}$	Benzene, 58.90 % + EtOH	$9.60 \cdot 10^{14}$	35 290	31 720	34 550	+ 7.6
$(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{COONa}$	Dioxan, 61.32 % + H_2O	$5.96 \cdot 10^{15}$	33 490	31 980	32 750	+ 2.1

DISCUSSION

When a molecule decomposes unimolecularly in the gaseous state to give radicals or atoms, the activation energy of the decomposition is equal to the energy of dissociation of the bond that is broken, provided the activation energy of the reverse reaction is zero ⁴.

As has been proposed previously ¹, the initial state of sodium tetrolate is characterized by a π_γ - and π_π -hyperconjugation between the methyl group and the triple bond, which decreases the potential energy of sodium tetrolate and at the same time retards its decarboxylation. The hyperconjugation is presumably of the same degree as in methylacetylene, *i. e.* a true hyperconjugation between the methyl group and the triple bond, since evidently conjugation does not occur between the triple bond and the carboxylate ion group in sodium tetrolate ². As the decomposing molecule enters the transition state, a partial negative charge develops at one end of the triple bond and prevents hyperconjugation to occur in the tetrolate ion. In order that the tetrolate ion can attain the same transition state structure as the propiolate ion, additional energy corresponding at least to the energy of hyperconjugation between the methyl group and triple bond is required in the case of the former in the gaseous state ¹. This is schematically shown in Fig. 1.

It is impossible to make measurements on the behaviour of ions in the gaseous state or even in non-polar solvents. An attempt has been made to approach the ideal conditions by conducting the decomposition reactions of the salts in aqueous and alcoholic solvents containing such proportions of non-polar components that the limits of precipitation of the salts are almost attained. Measurements on unimolecular reactions conducted in non-polar solvents are comparable with measurements conducted on such reactions in the gaseous state only if the initial state and the transition complex do not greatly differ from each other in structure. This condition appears to be fulfilled by the reactants under study, but since the purpose has been only to determine the activation energy difference, it is sufficient that the structures of the transition states of both the propiolate and tetrolate ions do not differ greatly. This appears to be true since the entropies of activation for the decompositions of these two compounds are only slightly different (Table 2). In fact the value of ΔS^* for sodium tetrolate is greater than that calculated for sodium propiolate,

Fig. 1. A schematic diagram showing Potential-Energy-Reaction-Coordinate curves for the decomposition of sodium propiolate and sodium tetrolate. The zero levels for the two compounds do not coincide.

which is explained by the hyperconjugation in the former. According to the view of solvation outlined previously², an ideal solvent for these compounds would be one that is unable to release and form hydrogen bonds at different solvation sites on the reacting molecule. On the other hand, observations made during the course of this study which are being studied in more detail, indicate that the solvent cannot be a hydrocarbon owing to the presence of the hydrocarbon chain in the decomposing compounds. Since carbon tetrachloride is unstable to alkalis, dioxan has been chosen as the non-polar solvent, particularly as it was found to conform with the requirements for an ideal solvent.

The variation of the activation energy for the decomposition reactions of sodium propiolate and sodium tetrolate with the composition of the solvent is shown in Fig. 2. It will be seen from the figure that the activation energy for sodium propiolate increases at first as the proportion of the non-polar solvent increases but, later on, decreases fairly steeply. The activation energy for sodium tetrolate, however, remains fairly constant with only a slight gradual rise over the solvent range. In the case of sodium propiolate an ideal limiting

Fig. 2. The variation of the activation energy with solvent composition for the decomposition of propiolate and tetrolate ions in various solvent mixtures. $\circ$ dioxan-water, Δ ethanol, $\square$ dioxan-ethanol, $\odot$ benzene-ethanol.

value appears to be attained when the limit of precipitation is approached, since the same value for the activation energy is found for the dioxan-water, ethanol-water and ethanol solutions. In the case of pure ethanol, sodium propiolate dissolves only with difficulty in this solvent to give a 0.02 *M* solution. As already mentioned, this precipitation limit could not be attained for sodium tetrolate in the case of the dioxan-water mixtures. However, the value found for the activation energy near the precipitation limit in the benzene-ethanol mixture appears to be the same as that which would be obtained by extrapolating the activation energy curve plotted for the reaction in the dioxan-water mixtures.

By subtracting the limiting value, 31 850 cal., of the activation energy for sodium propiolate from the corresponding value for sodium tetrolate, 35 290 cal., we obtain 3 440 cal. which is thus assumed to be the value of the hyperconjugation energy between a methyl group and a triple bond. This difference is believed to be accurate to ± 200 calories. To this experimental value, a further 1 100 cal. must be added as proposed by R. S. Mulliken and co-workers⁵ to take into account the fact that work must be done when the acceptor bond decreases and the donor bond increases in length in hyperconjugation against the forces which tend to maintain the normal lengths of the bonds. The resulting value for the theoretical hyperconjugation energy is thus 4 540 cal. Using the molecular orbital method, Mulliken and co-workers⁵ have theoretically calculated for the hyperconjugation energy in methylacetylene the value 4 520 cal. and on the basis of heats of combustion have obtained the experimental value $3\,600 \pm 200$ cal. which by adding the correction 1 100 cal. gives 4 700 cal. as the theoretical value. The accordance between these values and the value found in the present study is very satisfactory.

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