

## Hydrogen Bonding and Ionization of Methylene Hydrogen Adjacent to Carbonyl and Onium Groups

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Carbonyl compounds containing onium substituents on the carbon atom *alpha* to the keto group show strong activation of the methylene hydrogen atoms.

Infrared studies as well as measurements of the ionization of methylene groups adjacent to onium groups indicate that inductive and hyperconjugative effects are responsible for the activation.

The infrared absorption bands of the methylene stretching vibration have been localized by comparison of onium compounds containing undeuterated and deuterated  $\alpha$ -methylene groups.

In the solid state the methylene hydrogen atoms form hydrogen bond with the anion present in the onium salt. Relative to the vibration bands of methylene groups in hydrocarbons the methylene bands in onium compounds are in several cases displaced as much as  $200\text{ cm}^{-1}$  towards lower wave numbers. The displacement is coupled with a corresponding strong increase of band intensity. In analogously substituted onium salts the displacement and intensity of the methylene vibration bands are strongly dependent on the nature of the onium-forming element. The effects decrease in the order phosphonium > arsonium > sulphonium > ammonium.

The ionization of the methylene hydrogen atom of the onium salts in water and in ethanol water mixtures have been measured and are discussed in relation to inductive and hyperconjugative effects of the onium groups.

Normally, hydrogen atoms linked to carbon are able to form only very weak hydrogen bonds. The presence of strong electron acceptors adjacent to the C-H bond seems to be a necessary condition for hydrogen bond formation.<sup>1</sup>

In a previous paper<sup>2</sup> it was reported that carbonyl compounds containing a phosphonium group in  $\alpha$ -position to the keto group show very strong absorption bands in the region  $2600\text{--}2800\text{ cm}^{-1}$ . The position and intensity of the absorption bands were dependent on the anion present. In the case of triphenyl phenacyl phosphonium halides the bands were displaced towards lower wave numbers and higher intensities in passing from the iodide to the hydro-

gendifluoride. It was concluded that the absorption bands were due to hydrogen bond formation between the  $\alpha$ -methylene hydrogen atom and the anion. The ability of the methylene group to form hydrogen bond was assumed to be due chiefly to hyperconjugation involving a  $d$ -orbital of phosphorus.

This paper reports some further infrared studies of analogous onium compounds. The tendency for hydrogen bond formation of the methylene group in onium compounds is compared with its ability to ionize in water and in ethanol-water mixtures.

### EXPERIMENTAL

*Materials.* The onium compounds were synthesized from the corresponding amines, phosphines, arsines, and sulphides by treatment with  $\alpha$ -bromocarbonyl compounds.

1. *Trimethyl phenacyl ammonium bromide*, recrystallized from ethanol-ether, m.p. 215–216°. (Found: Br 30.92; 30.83. Calc. for  $C_{11}H_{16}NOBr$ : Br 30.96.)

2. *Trimethyl phenacyl phosphonium bromide*, recrystallized from ethanol-ether, m.p. 183–184°. (Found: Br 29.02; 29.12. Calc. for  $C_{11}H_{16}POBr$ : Br 29.05.)

3. *Dimethyl phenyl phenacyl phosphonium bromide*, recrystallized from chloroform-ethylacetate, m.p. 170–171°. (Found: Br 23.68. Calc. for  $C_{16}H_{18}POBr$ : Br 23.70.)

4. *Methyl diphenyl phenacyl phosphonium bromide*, recrystallized from chloroform-ethylacetate, m.p. 197°. (Found: Br 19.96. Calc. for  $C_{21}H_{20}POBr$ : Br 20.02.)

5. *Triphenyl phenacyl phosphonium bromide*, recrystallized from ethanol-ether, m.p. 287–288° (decomp.). (Found: Br 17.11; 17.19. Calc. for  $C_{26}H_{22}POBr$ : Br 17.32.)

6. *Triphenyl acetonyl phosphonium bromide*, recrystallized from chloroform-acetone, m.p. 227°. (Found: Br 19.76; 19.84. Calc. for  $C_{21}H_{21}POBr$ : Br 19.97.)

7. *Triphenyl p-bromophenacyl phosphonium bromide*, recrystallized from ethanol-ether, m.p. 192°. (Found: Br 14.58; 14.69. Calc. for  $C_{26}H_{21}POBr_2$ : Br 14.79.)

8. *Triphenyl carbethoxymethyl phosphonium bromide*, recrystallized from ethanol-ether, m.p. 155–156°. (Found: Br 18.47; 18.54. Calc. for  $C_{23}H_{22}PO_2Br$ : Br 18.62.)

9. *Trimethyl phenacyl arsonium bromide*, recrystallized from ethanol-ether, m.p. 186° (Found: Br 24.96. Calc. for  $C_{11}H_{16}AsOBr$ : Br 25.05.)

10. *Dimethyl phenyl phenacyl arsonium bromide*, recrystallized from acetone m.p. 176°. (Found: Br 21.11; 21.02. Calc. for  $C_{16}H_{18}AsOBr$ : Br 20.93.)

11. *Triphenyl phenacyl arsonium bromide*, recrystallized from ethanol-ether, m.p. 186° (Found: Br 15.45; 15.62. Calc. for  $C_{26}H_{22}AsOBr$ : Br 15.82.)

12. *Triphenyl p-bromophenacyl arsonium bromide*, recrystallized from ethanol-ether, m.p. 158°. (Found: Br 14.02; 13.89. Calc. for  $C_{26}H_{21}AsOBr_2$ : Br 13.78.)

13. *Dimethyl phenacyl sulphonium bromide*, recrystallized from chloroform-ethylacetate, m.p. 149°. (Found: Br 30.49; 30.58. Calc. for  $C_{10}H_{13}SOBr$ : Br 30.61.)

14. *Methyl phenyl phenacyl sulphonium bromide*, recrystallized from water, m.p. 103–104°. (Found: Br 24.82. Calc. for  $C_{15}H_{25}SOBr$ : Br 24.72.)

15. *Dimethyl p-bromophenacyl sulphonium bromide*, recrystallized from chloroform-ethylacetate, m.p. 143°. (Found Br 23.64; 23.58. Calc. for  $C_{10}H_{12}SOBr_2$ : Br 23.49.)

The corresponding methylene-deuterated onium compounds were obtained by boiling the onium salts in 99.8 % deuterium oxide for an appropriate time interval. The most acidic onium compounds ( $pK_a < 8$ ) were deuterated already on heating until dissolution, whereas the less acidic onium compounds ( $pK_a > 8$ ) were boiled 2–40 h depending on their  $pK_a$ -values. In order to obtain deuteration of the ammonium compound which has a  $pK_a$ -value above 10.5, it was necessary to add a small amount of sodium hydroxide as a catalyst. The deuterated compounds crystallized from the solution upon cooling or by slow evaporation of the solution.

The infrared spectra of the onium compounds were recorded as mulls in hexachlorobutadiene using an Unicam S. P. 100 instrument with NaCl-prism as well as grating optics.

The  $pK_a$ -values of the onium compounds were determined by potentiometric titration of a  $2.00 \times 10^{-3}$  M onium salt solution with a 0.05 M sodium hydroxide solution. In

two cases, the titration of triphenyl *p*-bromophenacyl phosphonium and arsonium bromides, the solutions were only  $1.00 \times 10^{-3}$  M due to the low solubility of the salts. The titration curves were obtained with a Radiometer Titrator (T.T.T.I.C.) at 20°C. The  $pK_a$  of the onium compounds in various ethanol water mixtures (Table 1) are values relative to water in so far as the glass electrode was calibrated against a standard sodium hydrogenphosphate buffer in water. The absolute  $pK_a$ -values for the ionization in ethanol water mixtures must therefore be assumed to be considerably higher.

### THE METHYLENE VIBRATION IN ONIUM SALTS

Localization of the stretching vibration of the methylene group in the various solid onium salts was achieved by comparison of the infrared spectra of onium compounds containing undeuterated and deuterated methylene groups. In Fig. 1 is shown the infrared spectra of undeuterated and deuterated

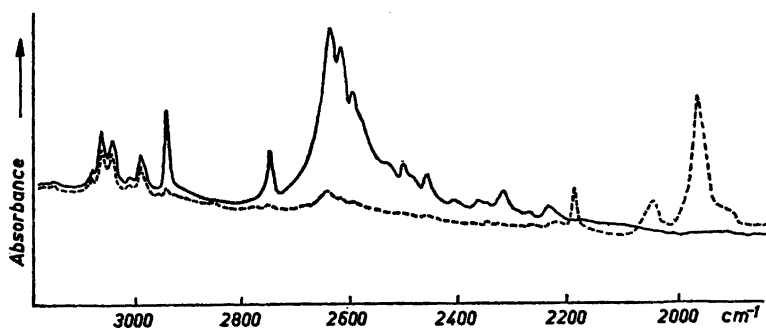
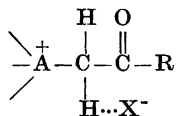


Fig. 1. Infrared spectra of undeuterated (—) and deuterated (---) triphenyl phenacyl phosphonium bromide in hexachlorobutadiene.

triphenyl phenacyl phosphonium bromide in the region 3100–1900  $\text{cm}^{-1}$ . The peaks at 2938, 2750, and 2638  $\text{cm}^{-1}$  in the undeuterated compound correspond to the peaks 2183, 2032, and 1952  $\text{cm}^{-1}$  in the deuterated compound. The isotope ratio for the stretching vibrations is thus 1.35 for all three pairs of bands. By this method at least two main absorption bands were localized for the methylene stretching vibration in all of the onium compounds studied. In some cases three bands were observed (*cf.* Table 1).

As concluded in a previous paper,<sup>2</sup> the infrared absorption spectra of the solid onium salts indicates hydrogen bond formation between a methylene hydrogen atom and the halide ion:



The hydrogen bonding explains the increasing displacement of the stretching vibration bands of the methylene group towards lower frequencies, as well as their increasing intensities, in the order  $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{HF}_2^-$ .<sup>2</sup> Studies

Table 1. The C-H stretching vibrations of deuterated and undeuterated  $\alpha$ -methylene groups in onium bromides. Me = methyl, Et = ethyl, Ph = phenyl, PhBr-*p* = *p*-bromophenyl.

No.	Compound	Stretching vibration ( $\text{cm}^{-1}$ )		Isotope ratio C-H/C-D
		-CH <sub>2</sub> -	-CD <sub>2</sub> -	
1	Me <sub>3</sub> <sup>+</sup> NCH <sub>2</sub> COPh	2951	2222	1.33
		2921	2135	1.36
2	Me <sub>3</sub> <sup>+</sup> PCH <sub>2</sub> COPh	2891	2148	1.34
		2847	2089	1.36
3	(Me) <sub>2</sub> <sup>+</sup> PhPCH <sub>2</sub> COPh	2851	2138	1.33
		2827	2082	1.36
4	Me(Ph) <sub>2</sub> <sup>+</sup> PCH <sub>2</sub> COPh	2840	2122	1.34
		2780	2063	1.35
5	Ph <sub>3</sub> <sup>+</sup> PCH <sub>2</sub> COPh	2938	2183	1.35
		2750	2032	1.35
		2638	1952	1.35
6	Ph <sub>3</sub> <sup>+</sup> PCH <sub>2</sub> COMe	2805	2114	1.33
		2782	2047	1.36
7	Ph <sub>3</sub> <sup>+</sup> PCH <sub>2</sub> COPhBr- <i>p</i>	2921 (?)	2130	1.37
		2795	2069	1.35
		2722	2000	1.36
8	Ph <sub>3</sub> <sup>+</sup> PCH <sub>2</sub> COOEt	2811	2120	1.33
		2750	1997	1.37
9	Me <sub>3</sub> <sup>+</sup> AsCH <sub>2</sub> COPh	2918	2200	1.33
		2868	2110	1.36
10	(Me) <sub>2</sub> <sup>+</sup> PhAsCH <sub>2</sub> COPh	2887	2176	1.33
		2852	2096	1.36
11	Ph <sub>3</sub> <sup>+</sup> AsCH <sub>2</sub> COPh	2955	2214	1.33
		2762	2030	1.36
		2660	1960	1.36
12	Ph <sub>3</sub> <sup>+</sup> AsCH <sub>2</sub> COPhBr- <i>p</i>	2920	2200	1.33
		2810	2060	1.36
		2730	2000	1.36
13	Me <sub>2</sub> <sup>+</sup> SCH <sub>2</sub> COPh	2949	2216	1.33
		2900	2127	1.36
14	(Me)Ph <sup>+</sup> SCH <sub>2</sub> COPh	2911	2195	1.33
		2860	2085	1.37
15	Me <sub>2</sub> <sup>+</sup> SCH <sub>2</sub> COPhBr- <i>p</i>	2918	2203	1.33
		2865	2165	1.32

of the infrared spectra of the onium salts in chloroform and acetonitrile solutions revealed no such unusual methylene absorption. Presumably, the hydrogen bond between the methylene group and the solvent is too weak to be detected.

According to Fox and Martin<sup>3</sup> the vibrations of the methylene group in aliphatic hydrocarbons give rise to two bands in the infrared, at 2926 and 2853  $\text{cm}^{-1}$ , corresponding to the in-phase and out-of-phase vibrations of the hydrogen atoms. As seen from Table 1 a methylene group adjacent to a carbonyl and a methyl substituted ammonium group gives rise to methylene vibrations of higher wave numbers than the aliphatic hydrocarbons. In analogous phosphonium and arsonium compounds, however, the methylene bands are located at wave numbers very much lower than in aliphatic hydrocarbons. The observations suggest that at least two opposing electronic effects, inductive and hyperconjugative respectively, influence the positions of the infrared absorption bands. There are several examples that strongly electron accepting atoms (chlorine, oxygen, sulphur) adjacent to methyl and methylene groups displace the methyl and methylene bands towards higher frequencies.<sup>4</sup> Since the ammonium group has electron accepting character only, ( $-I$ ), its influence on an adjacent methylene group should be in the direction observed. Onium groups of elements from the second and third periods (phosphorus, sulphur, arsenic) have  $d$ -orbitals available for bonding.<sup>5</sup> The strong displacement of the methylene vibrations towards lower frequencies coupled with the strong increase of absorption intensity exerted by the latter onium groups (Table 1) are most reasonably due to hyperconjugation involving the  $d$ -orbitals.

Replacement of an electron donating methyl group, ( $+I$ ), by an electron withdrawing phenyl group, ( $-I$ ), increases the positive charge on the onium group. This will, according to Craig *et al.*<sup>5</sup>, make the  $d$ -orbitals more suitable for bonding. From Table 1 is seen that such substitution (*cf.* compounds Nos. 2, 3, 4, 5, 9, 10, 11, 13, and 14) gives rise to a displacement of the absorption bands in the expected direction (towards lower frequencies).

The inductive effect of onium groups depends on the atomic radii of the elements and decreases in the order,  $\text{N} > \text{S} > \text{P} > \text{As}$ . Utilization of  $d$ -orbitals for bonding is most pronounced in the second period. On this background the stronger influence of the phosphonium group on the methylene vibrations, as compared with other onium groups, is reasonable. In the analogous sulphonium compounds the hyperconjugative effect is counteracted by a stronger inductive effect, and the methylene vibrations are accordingly located at higher frequencies. The lone pair of electrons in the sulphonium group may also be of significance in this respect.

#### IONIZATION OF ONIUM SALTS IN WATER AND IN ETHANOL-WATER MIXTURES

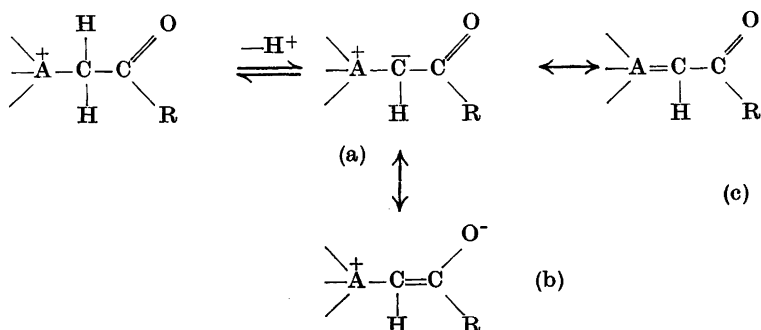
The hydrogen atoms in methylene groups containing adjacent carbonyl and onium substituents are sufficiently activated to give measureable ionization in water and in ethanol-water mixtures.

As pointed out by several workers,<sup>2, 6-9</sup> the strong acidifying effect of onium groups of the second and third periods can be ascribed to the utili-

Table 2.  $pK_a$ -values for the ionization of the  $\alpha$ -methylene hydrogen in various onium bromides. Temp. 20°C.

No.	Compound	$pK_a$ -values in various ethanol-water mixture (% ethanol by weight)				
		0	25	35	50	80
1	$\text{Me}_3\text{N}^+\text{CH}_2\text{COPh}$	<i>ca.</i> 10.5	—	—	—	—
2	$\text{Me}_3\text{P}^+\text{CH}_2\text{COPh}$	9.20	9.10	—	9.05	9.00
3	$(\text{Me})_2\text{Ph}^+\text{PCH}_2\text{COPh}$	8.45	8.00	—	8.05	8.15
4	$\text{Me}(\text{Ph})_2\text{P}^+\text{CH}_2\text{COPh}$	7.65	7.35	—	7.10	6.85
5	$\text{Ph}_3\text{P}^+\text{CH}_2\text{COPh}$	—	6.65	6.45	6.15	6.00
6	$\text{Ph}_3\text{P}^+\text{CH}_2\text{COMe}$	7.55	7.50	—	7.30	6.65
7	$\text{Ph}_3\text{P}^+\text{CH}_2\text{COPhBr-}p$	—	6.10	5.95	5.60	5.40
8	$\text{Ph}_3\text{P}^+\text{CH}_2\text{COOEt}$	<i>ca.</i> 10.5	9.80	—	9.10	8.85
9	$\text{Me}_3\text{As}^+\text{CH}_2\text{COPh}$	9.15	9.20	—	9.50	10.20
10	$(\text{Me})_2\text{Ph}^+\text{AsCH}_2\text{COPh}$	8.45	8.75	—	9.20	9.85
11	$\text{Ph}_3\text{As}^+\text{CH}_2\text{COPh}$	—	8.90	8.75	8.55	8.65
12	$\text{Ph}_3\text{As}^+\text{CH}_2\text{COPhBr-}p$	—	7.80	8.10	8.00	7.90
13	$\text{Me}_3\text{S}^+\text{CH}_2\text{COPh}$	8.25	8.25	—	8.30	8.45
14	$(\text{Me})\text{Ph}^+\text{SCH}_2\text{COPh}$	7.45	7.30	—	7.20	7.20
15	$\text{Me}_2\text{S}^+\text{CH}_2\text{COPhBr-}p$	—	7.80	—	7.80	7.60
	Sodium phosphate buffer	6.50	7.27	7.40	—	—

zation of  $d$ -orbitals for  $\pi$ -bonding in the base formed as a result of the ionization process. Since the ionization depends upon the structures of the onium salt as well as its corresponding base, the ionization is quite different from the light absorption which depends upon the structure of the undissociated salt only. In the latter case the  $d$ -orbitals of the onium group can only be utilized for hyperconjugation, whereas in the former case hyperconjugation in the onium salt as well as conjugation in the corresponding base will contribute to the total picture of ionization:



The stronger the inductive effect of the onium group, the greater will be the contribution from the ionic structures of the base. Since the intensity of the electric field around the onium atoms depends upon their radii, the tendency for ylid structure (a) and (b) of the bases should decrease in the order,  $N > S > P > As$ . Ionization in strongly polar media should accordingly be more favoured for ammonium and sulphonium salts than for phosphonium and arsonium compounds. The ylene structure, (c) is dependent upon participation of *d*-orbitals and is expected to be most pronounced for bases from the onium salts of the second period. Since the ylene structure neutralizes the charge separation in the base, the dissociation of onium compounds will on this basis be favoured by decreasing polarity of the solvent. Depending upon the importance of ylid and ylene structure, the ionization of the onium compounds should thus decrease or increase respectively, on passing from water to ethanol-water mixtures. The relative  $pK_a$ -values recorded in Table 2 seem to indicate that the importance of the ylene structure is greatest for phosphonium and sulphonium salts, since their relative  $pK_a$ -values decrease with increasing ethanol content of the solvent (except for the dimethyl sulphonium compound where there is a small increase in the  $pK_a$ -value). The stronger ionization of dimethyl phenacyl and methyl phenyl phenacyl sulphonium bromide as compared with the corresponding phosphonium salts (compounds Nos. 2, 3, 13, and 14) can be ascribed to the greater inductive effect of the sulphonium group.

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