THE EFFECT OF ALKYL SUBSTITUTION ON THE SPECTRA AND IONIZATION POTENTIALS OF SOME FUNDAMENTAL CHROMOPHORES[1]

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The effect of alkyl substitution on the ionization potentials of electrons in chromophoric groups is illustrated by an extensive collection of best values. Thermochemical data are used to show that the reductions in ionization potential which accompany alkyl substitution are due to a relatively large stabilization of the molecular ion accompanying the introduction of the additional alkyl group. Although small stabilization of the unexcited neutral molecule occurs on alkyl substitution, this is of a lower order of magnitude than that associated with the ionic state. The greater relative stabilization of the molecular ion is implicit in the theory of hyperconjugation, but the effects observed seem to be larger than can be accounted for on the simple hyperconjugation theory. It is thought that various charge-transfer effects occurring in the ionic state are responsible for a great part of the reduction. The red shifts of many absorption bands on alkyl substitution are no doubt to be attributed, at least in part, to similar causes.

The wave length at which an absorption band occurs depends upon the difference between the energies of the ground and the excited states of the molecule absorbing the radiation. Any attempt to understand the wave-length shifts produced by different substituents in a chromophore must therefore take into consideration the effect of the substituent on the energies of both the upper and the lower states associated with the transition. For example, if the substitution of an alkyl group into benzene were found to increase the resonance energy of the ground state relative to that of benzene itself, it would still be necessary to know the change in the resonance energy of the excited state before the shift in the absorption band could be predicted. Conversely, the change in resonance energy or stability of the excited state can be predicted if the shift in the absorption band and the change in resonance energy of the normal state resulting from the substitution are known. In order to simplify matters somewhat it is convenient to consider first the ionization potentials of substituted molecules instead of their absorption spectra, since then it is only necessary to take into account the energies of the normal and the ionized states, and the difficulty of assessing the bonding or antibonding contribution of the excited electron is avoided. Table 1 contains a classified list of the ionization potentials of a large number of molecules which can be considered as derived from the first member of each class by alkyl substitution.

The values given in table 1 are in general believed to be accurate to within half

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TABLE 1

Table showing the effect of substitution on ionization potential

SUBSTANCE	IONIZATION POTENTIAL	REFERENCES
Hydrocarbons		
Hydrogen	15.427	(2, 32)
Methane	13.1	(33)*
Ethane	11.6	(8)*
Propane	11.3	(5)*
n-Butane and isobutane	10.34	(9)*
Hydrogen atom	13.595	(4)
Methyl radical	10.07	(10)*
Ethyl radical	8.67	(10)*
n-Propyl radical	7.80	(7)*
Isopropyl radical	7.77	(7)*
tert-Butyl radical	7.19	(7)*
Ethylene	10.50	(26)
Propylene	9.70	(9, 26)*
1-Butene	9.65	(35)*
2-Butene	9.24	(26)
Isobutene	8.95	(37)*
Trimethylethylene	8.80	(26)+
Tetramethylethylene	8.30	(26)+
Butadiene	9.07	(27)
β-Methylbutadiene	8.86	(27)
β,γ-Dimethylbutadiene	8.72	(27)
Benzene	9.24	(30)
Toluene	8.92	(29)
Ethylbenzene	*ca.* 8.75	Unpublished data +
Isopropylbenzene	*ca.* 8.6	Unpublished data +
tert-Butylbenzene	*ca.* 8.5	Unpublished data +
o-Xylene	*ca.* 8.3	Unpublished data +
m-Xylene	*ca.* 8.3	Unpublished data +
p-xylene	*ca.* 8.3	Unpublished data +
Naphthalene	8.3	(4)*
β-Methylnaphthalene	8.0	Unpublished data +
Acetylene	11.41	(21)
Methylacetylene	11.30	(28)
Alkyl derivatives of H_2O, H_2S, NH_3, HCHO, and the halogen acids		
Water	12.61	(23)
Methyl alcohol	10.8	(38)*
Ethyl alcohol	10.7	(38)*
Propyl alcohol	10.7	(38)*
Dimethyl ether	10.5	(38)*
Diethyl ether	10.2	(38)*
Hydrogen sulfide	10.47	(23)
Ethyl mercaptan	9.70	(38)*

TABLE 1—*Continued*

SUBSTANCE	IONIZATION POTENTIAL	REFERENCES
Dimethyl sulfide	9.40	(38)*
Diethyl sulfide	9.30	(38)*
Di-*n*-propyl sulfide	9.20	(38)*
Ammonia	10.8 (11.5)	(38)
Methylamine	9.8	(38)*
Dimethylamine	9.6	(38)*
Trimethylamine	9.4	(38)*
Formaldehyde	10.88	(22)
Acetaldehyde	10.23	(40)
Acetone	10.1	(18)
Hydrogen chloride	12.84	(25)+
Methyl chloride	11.25	(24)
Ethyl chloride	10.89	(24)+
n-Propyl chloride	10.7	(36)*
tert-Butyl chloride	10.2	(36)*
Hydrogen bromide	12.04	(25)+
Methyl bromide	11.17	(24)
Ethyl bromide	10.92	(24)
Hydrogen iodide	10.33	(25)
Methyl iodide	9.49	(24)
Ethyl iodide	9.34	(24)
Halogen-substituted hydrocarbons		
Ethylene	10.50	(26)
Vinyl chloride	10.00	(26)
cis-Dichloroethylene	9.66	(39)
trans-Dichloroethylene	9.96	(39)
Butadiene	9.07	(27)
Chloroprene	8.83	(27)
Benzene	9.24	(30)
Monochlorobenzene	8.8	(29)

a unit of the last figure given. In some cases, particularly that of the alkyl radicals, the error may be four or five times greater than this. The values determined from Rydberg series have been recalculated, using the conversion factor based upon the new value of the elementary charge. The electron-impact values have been given as quoted by the original author, as the increase of 0.5 per cent due to the new value of *e* is usually within the experimental error. Some ionization potentials have been estimated by considerations of spectroscopic features other than Rydberg series. These are marked +. In the case of unsaturated and aromatic hydrocarbons the electron removed is a π double-bond electron. For the other molecules the ionization is of a non-bonding electron, usually $p\pi$, localized on the nitrogen, oxygen, sulfur, or halogen atom, respectively. Electron-impact values are starred.

From the table it is clear that the substitution of a hydrogen atom by an alkyl group always has the effect of lowering the ionization potential. The amount of the lowering depends, among other things, upon the proximity of the alkyl group to the electron affected. What is considered to be most important in this connection, however, is the fact that the magnitudes of the changes, which are often of the order of 0.5 volt or 10 kcal. per mole, are far greater than any changes in ground-state stabilization (resonance energy) which have been shown by heats of hydrogenation or formation to accompany substitution. The conclusion to be drawn from this is that the main cause of the reduction is to be sought for in an increase in the stability of the molecular ion resulting from the substitution.

TABLE 2

Stabilization energy and reduction of ionization potential of alkylethylenes relative to ethylene (in kilocalories per mole)

SUBSTANCE	ΔC	ΔH	ΔI
Propylene	3.032	2.7	18.4
1-Butene	2.639	2.5	23.0
2-Butene (*cis*)	4.281	4.2	21.5
2-Butene (*trans*)	5.320	5.2	*ca.* 21.0
2-Methylpropene ("isobutene")	4.620	4.4	35.7
Trimethylethylene	5.970	5.8	39.2
Tetramethylethylene	6.140	6.2	49.5

MONOÖLEFIN HYDROCARBONS

The class of molecules for which the thermal data are most complete is the monoölefin hydrocarbons, and these will therefore be considered first. Table 2 gives the heats of stabilization relative to ethylene of the various alkylethylenes as obtained from heats of combustion (ΔC) (17) and hydrogenation (ΔH) (12), together with the diminutions in ionization potential of the π electrons, all quantities being expressed in kilocalories per mole. The ΔC's of table 2 were calculated in the following manner from heat of combustion data given in the A.P.I. tables (17):

$$\Delta C = \{C\text{ (satd.)} - C\text{ (unsatd.)}\} - \{C\text{ (ethane)} - C\text{ (ethylene)}\}$$

where C (satd.) is the heat of combustion of the corresponding saturated hydrocarbon. It is obvious that ΔC should be equal to ΔH from this equation, since H is equal to the heat of formation of 1 mole of water minus $\{C\text{ (satd.)} - C\text{ (unsatd.)}\}$. The agreement between the two sets of values, which does not appear to have been previously pointed out, is very satisfactory. The fact that the C's are referred to a temperature of 25°C. and the heats of hydrogenation to 82°C. has negligible effects on this agreement, as can be shown by calculating the heats of combustion for the higher temperature from the extensive data of Rossini and collaborators (17).

The agreement between the ΔH's and ΔC's is incidental to the point being stressed here and is only given to show that the thermochemical values obtained for the stabilizations by alkyl substitution of the monoölefin hydrocarbons in their ground states are well founded. The important fact contained in table 1 is that the changes in ionization potential are much larger than the increases in stabilization of the normal states of the molecules. They are, in fact, in the opposite direction from what would be expected if the normal state alone and not the ionic state were affected by the substitution. The explanation must be that while both normal and ionized states are stabilized, the ionic state is stabilized to a relatively much greater extent. Thus, while the normal state of propylene has a stabilization energy of 3 kcal. per mole relative to ethylene, its ionic state is stabilized by as much as 21 relative to $C_2H_4^+$. Such stabilization of the ion is implicit in the molecular orbital description of the hyperconjugation effects produced by the alkyl substitution, but it is not certain whether the whole of the stabilization can be accounted for by hyperconjugation alone. Consider the case of propylene. Suppose the term value of the double-bond π electrons is E_2 and that for the quasi $\pi(CH_3)$ electrons is E_1, these values being roughly equal to the ionization potential of the unbound electron plus its contribution to the energy of the bond (β_2, β_1). Then the interaction of these π orbitals will lead to a lowering of E_2 by ϵ_2 and a raising of E_1 by ϵ_1. Thus, the stabilization energy of propylene relative to ethylene arising out of hyperconjugation is $2(\epsilon_1 - \epsilon_2)$, while the first ionization potential has dropped by an amount ϵ_2 and the ion is stabilized by an amount $(\epsilon_1 - \epsilon_2) + \epsilon_1$. For propylene $2(\epsilon_1 - \epsilon_2) = 3$ kcal. and $\epsilon_2 = 18.4$ kcal., hence $\epsilon_1 = 19.9$ kcal. Now, the magnitudes of ϵ_1 and ϵ_2 would not be expected to be more than 10–20 per cent of the values β_1 and β_2, as the changes arising from full conjugation as in butadiene are only about 40 per cent β. On this hypothesis the magnitudes of β_1 and β_2 would be expected to be roughly 100–150 kcal. The old value for β_2 used to be about 18 kcal., later being stepped up to 35 kcal. (13). However, Professor R. S. Mulliken thinks that it might be raised to as much as 70 kcal. Unless

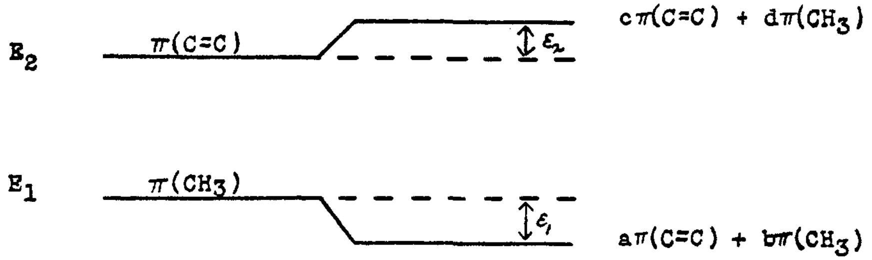


FIG. 1. Effect of hyperconjugation on the binding energies of the double bond and methyl "π" electrons in propylene.

this high value for β_2 is substantiated, it appears that some additional effect will have to be postulated to explain the large reductions in ionization potential in going from ethylene to propylene. It should be mentioned, however, that the red shifts of the alkylethylenes in their 1800 A. bands appear to be completely accounted for in terms of hyperconjugation (16). The author believes that an additional effect which brings about stabilization of the molecular ion may be in the nature of a charge transfer which comes into operation on the excitation or ionization of an electron. It is assumed that any charge transfer which occurs in the normal, excited, or ionized state brings about stabilization by resonance to ionic structures. In the case of the normal state of propylene charge can only migrate into the double bond by making use of the $(x - x)$ or higher occupied orbitals. However, in the ion charge can flow into the low $x + x$ orbital which has been vacated. Much more charge can flow in this case than in that of the neutral molecule and much greater stabilization can thereby be produced. While the polar state of the normal molecule, *viz.*,

$$\mathrm{H_3^+\overset{\cdot}{=}C{-}CH^-\overset{\cdot}{=}CH_2}$$

is an improbable one, the polar state of the ion, $\mathrm{H_3^+\overset{\cdot}{=}C{-}CH{=}CH_2}$, is much more likely and probably makes a considerable contribution to the stability of the $\mathrm{H_3{\equiv}C{-}CH^+\overset{\cdot}{-}CH_2}$ ion. The fact that the more highly excited shorter-wave-length absorption bands suffer larger shifts on substitution than do the longer-wave-length bands of a molecule also fits in with the above explanation, since it is to be expected that the more completely an electron is removed the greater will be the ensuing charge migration.

The above idea can be expressed in terms of molecular orbital theory in the following way: Firstly, it should be stated that a certain amount of charge transfer for the ion is contained in the idea of hyperconjugation. If there were no hyperconjugation, then on ionization the double bond would lose one electron. However, as a result of the hyperconjugation it only loses a fraction of an electron, the amount depending on the coefficients a and b in the mixed orbital $a\phi(\pi, \mathrm{C{=}C}) + b\phi(\pi, \mathrm{CH_3})$. The corresponding orbital for the quasi $\pi\mathrm{CH_3}$ electrons can be written $c\phi(\pi, \mathrm{C{=}C}) + d\phi(\pi, \mathrm{CH_3})$, where $d \gg c$ in the ground state. It is thought that in the ionized state c will increase considerably as a result of the increase in electron affinity of the ethylenic bond on ionization and this will result in the sort of charge transfer described above. Such an additional charge transfer would not be expected where there is complete conjugation as in butadiene, as both double bonds would be equally affected and there would be no change in the mixing coefficients.

ALKYLBENZENES

Another set of molecules for which thermochemical data are available on the effect of substitution of the normal states is that of the alkylbenzenes (17). The heats of hydrogenation diminish with substitution as in the alkylethylenes, but the stabilization produced is not quite so great as in the former class of molecules, possibly because of the resonance stabilization already present. However, judged from a criterion given in a later section, *viz.*, that stabilization energy = 157.4 − {C (RX) − C (HX)}, which takes some account of paraffinoid as well as resonance stabilization, the effect in aromatics (*ca.* 2.9 kcal.) is much more comparable with that in olefins (*ca.* 2.65 kcal.), both being about half the value found for the acetylenes (4.8 kcal.). The available hydrogenation data obtained in a manner similar to that used for table 2 are given in table 3.

It will be noted that both ΔH and ΔI are smaller than for the alkylethylenes. As explained in connection with the alkylethylenes, the effect of the hyperconjugation is to lower the ionization potentials of the aromatic π electrons and to increase that of the quasi πCH_3 electrons, yielding a resultant stabilizing energy of the ground state and a much greater stabilization of the molecular ion. The explanation of the relatively greater stabilization of the molecular ion follows essentially the same lines as that already given for the ethylene derivatives. Firstly, a large proportion of it is explicable in terms of ordinary ideas of hyperconjugation. Secondly, there may be a further charge-transfer effect arising out of the migration of methyl electrons into the low orbital of the ring which has been vacated by the electron which has been ionized. This latter effect may be the same thing as saying that the molecular orbitals in the ion differ from those in the neutral molecule by having the mixing coefficient of the aromatic π orbital increased relative to that of the alkyl π orbital as a result of the increased electronegativity produced in the ring by the ionization. In the normal molecule resonance between the aromatic and alkyl π electrons is limited by the fact that their energies are considerably different, their ionization potentials being *ca.* 9 and 12 volts, respectively. In the ion, which has lost an aromatic π electron, the ionization potential may be much more evened out by the relatively greater increase of the ionization potential of the ring electrons compared to those of the substituent and both may now require, for instance, *ca.* 20 volts for their removal. This increased resonance leads to increased stabilization of the ion and implies considerable charge transfer from the methyl radical to the ring.

TABLE 3

Stabilization energy and reduction of ionization potential of alkyl aromatics relative to benzene (in kilocalories per mole)

SUBSTANCE	ΔC	ΔH	ΔI
Toluene	0.30		9.7
Ethylbenzene	1.16	0.9	*ca.* 11.3
n-Propylbenzene	1.17		*ca.* 14.7
n-Butylbenzene	1.59		
n-Pentylbenzene	1.59		
n-Hexylbenzene	1.59		
o-Xylene		2.5	*ca.* 18.0
Mesitylene		2.2	*ca.* 25.0

The differences of ionization potential in the pairs ethylene–propylene, benzene–toluene, and acetylene–methylacetylene are 0.80, 0.42, and 0.11 volt, respectively. The low value of the difference between acetylene and methylacetylene means that the methylacetylene ion is not preferentially stabilized to any great extent by the resonance charge-transfer effects referred to above. This is understandable qualitatively, as it is known that such charge transfer occurs to a considerable extent in the ground state of the molecule and the amount of additional charge transfer that can take place in the ion is therefore somewhat limited.

All *NV* bands of the alkylbenzenes are stronger than they are in benzene itself, indicating hyperconjugation (16). This involves a charge transfer, the effect of which may be enhanced by an alteration of the mixing coefficients for the aromatic and alkyl π orbitals in the excited state as suggested for the ions. The f values found for the xylenes (20) are greater than unity, presumably because some of the intensity is drawn from the alkyl π electrons. Only the Rydberg bands appear to lose intensity, and this may be because they are blurred out by predissociation or other effects.

It should be pointed out that extensive resonance can often occur without it being apparent from thermochemical data. For example, the heat of hydrogenation of styrene is very little different from that calculated for the isolated aromatic and ethylenic double bonds. However, it is obvious from the spectra that there is intimate mixing between the aromatic and ethylenic orbitals which are very considerably affected by the resonance. The resonance energy in the ground state is a net effect which might well change only slightly, though the contributing factors alter appreciably.

SATURATED PARAFFINS

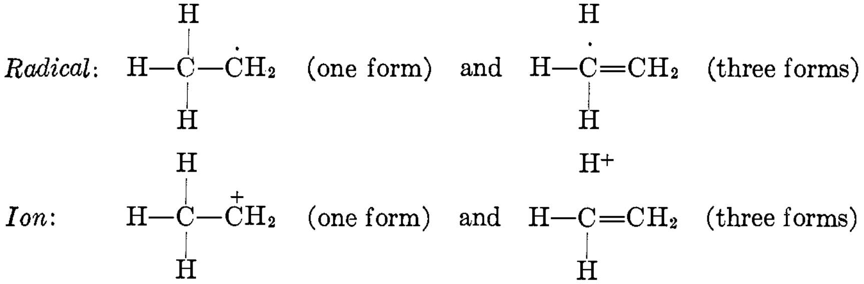
The next set of molecules to be considered are the saturated hydrocarbons. It is not possible to assign energy values to one class of electrons in this case in the same way that heats of hydrogenation can be associated with double-bond electrons in olefins and aromatics. However, in a crude approximation we only have to deal with electrons in single C—H and C—C bonds. This is not strictly the case, as is brought out by Mulliken's molecular orbital treatment (14). To a first approximation the ionization potential and absorption spectra of methane can be attributed to electrons in C—H bonds. For ethane and higher hydrocarbons, the lowest ionization potentials are taken to be those of electrons in C—C bonds. It is seen from table 1 that lowering of the ionization potential occurs with increased number of C—C bonds. This is probably to be related to the fact that an increasing number of bond structures can be written for the molecular ion with increase in the number of carbon atoms it contains. Thus $C_2H_6^+$ has one structure, $C_3H_8^+$ has two, $C_4H_{10}^+$ has three, and so on. The more highly branched a substance is the more of these structures become equivalent, causing further stabilization which may be reflected in the ionization potential. Taking into account charge transfer, two more structures of the type

$$H_3^+ \dot{=} C - C \equiv H_3$$

must be considered for $C_2H_6^+$, three for $C_3H_8^+$, four for $C_4H_{10}^+$, etc., and no doubt these contribute appreciably to the stability of the ion. Stabilization by branching appears to be somewhat offset by comparable stabilization occurring in the ground state. Thus the electron-impact experiments of Hipple and Stevenson (9) were unable to detect appreciable differences between the ionization potentials of *n*-butane and isobutane.

ALKYL RADICALS

The possible variation in the ionization potentials of different radicals arising from different amounts of resonance energy in the normal and ionized states was considered by Baughan, Evans, and Polanyi (1). They wrote the following structures as possible resonance forms of the ethyl radical and its ion



$$\textit{Radical}:\quad \mathrm{H{-}\underset{\displaystyle H}{\overset{\displaystyle H}{C}}{-}\dot{C}H_2}\ \text{(one form) and }\ \mathrm{H{-}\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{\cdot}{C}}}{=}CH_2}\ \text{(three forms)}$$

$$\textit{Ion}:\quad \mathrm{H{-}\underset{\displaystyle H}{\overset{\displaystyle H}{C}}{-}\overset{+}{C}H_2}\ \text{(one form) and }\ \mathrm{H{-}\underset{\displaystyle H}{\overset{\displaystyle H^+}{C}}{=}CH_2}\ \text{(three forms)}$$

and concluded on the basis of these structures that the resonance in the radical and in the ion are comparable and that there should not be much difference in the ionization potentials of the methyl, ethyl, isopropyl, or *tert*-butyl radicals. The resonance in the ethyl radical was computed to be only about 7 kcal.; that of the isopropyl and tertiary butyl radicals (resonance among seven and ten forms, respectively) was computed to be somewhat greater, but the authors concluded that the ionization potentials of the various radicals did not differ greatly because in all cases the resonance energy of the ion did not appear to be very different from that of the normal state of the molecule. It was subsequently shown by experiment (7, 10) that there is a great deal of variation amongst these ionization potentials. The explanation of this appears to be fairly clear in terms of the concepts already outlined and is as follows: There is much greater stabilization of the ethyl ion by virtue of the hyperconjugation of the quasi π orbitals of the methyl group with the vacated π orbital of the methylene group.

$$\mathrm{H_3{\equiv}C{-}\overset{+}{C}{=}H_2} \qquad \mathrm{H_3^+{\stackrel{\cdot}{=}}C{-}\overset{\cdot}{C}{=}H_2}$$

This incidentally results in considerable charge transfer from the methyl group into the methylene group by hyperconjugation, an effect which does not occur to nearly the same extent in the neutral radical. Thus, the ion is stabilized considerably relative to the neutral ethyl radical and this reduces its ionization potential compared to that of the methyl radical, whose ion is not stabilized by the same process. On the molecular orbital theory the ethyl radical is somewhat similar to the three-center problem discussed by Hückel (11), who considers the allene radical. It differs in so far as the quasi π and ethylenic $p\pi$ orbitals are not equivalent. Hückel's simple treatment leads to one strongly bonding, one non-bonding, and one antibonding molecular orbital. In the ethyl radical these may be thought of as the bonding π (CH_3) orbital depressed by resonance with the ethylenic $p\pi$, the antibonding orbital elevated (or made more antibonding) from the same cause, and the non-bonding ethylenic orbital remaining unchanged as a result of mutually opposing effects from the two orbitals already mentioned. In practice, it appears that the depressing effect of the antibonding orbital is considerably less than the elevating effect of the bonding orbital, so that the non-bonding orbital becomes appreciably antibonding. In the neutral radical two electrons would occupy the first orbital and one would have to go into the slightly antibonding orbital. This last electron would be the one corresponding to the first ionization of the radical. The radical ion is stabilized because the remaining electrons are in fully bonding orbitals. Further, as a result of the ionization, which is mainly located in the CH_2 group, there will be an adjustment in the mixing coefficients of the bond orbitals and additional charge transfer and stabilization are to be expected from this effect.

Another explanation of the low ionization potentials of the radicals which has to be considered is connected with the possibility that the radicals might be bent in their normal states (like ammonia and the amines) and might acquire a more stable planar configuration on ionization, the repulsion between methyl groups bound to a tetrahedral carbon being less when they are in a planar configuration bound to a trigonal C^+. However, it appears that the energies of the in-plane and out-of-plane configurations only differ by a small fraction of a volt (as can easily be shown to be true in the case of ammonia). Also, the packing of many methyl groups on to a carbon atom actually has a stabilizing and not a destabilizing influence, as indicated by the fact that the heats of combustion of branched-chain hydrocarbons are always a few kilocalories less than those of straight-chain hydrocarbons. Finally, the ionization potentials of the radicals run very closely parallel to, and roughly 3 volts less than, those of the corresponding hydrocarbons where there is little probability of change in geometrical shape on ionization. As a result, it is felt that such a change cannot have a major effect upon the ionization potentials of the radicals and the changes which do occur are not fundamentally very different from those which give rise to the reductions in ionization potential of the saturated hydrocarbons.

Rough values for the relative stabilization of the normal and ionized states of the radicals can be obtained from the data on the alkyl iodide bond strengths quoted by Evans (7) The energy required to dissociate the alkyl iodide into radical and iodine atom is given as 54 kcal. per mole for methyl iodide, 52 for ethyl iodide, 50 for *n*-propyl iodide, 46.5 for isopropyl iodide, 49 for *n*-butyl iodide, and 45 for *tert*-butyl iodide. Assuming this variation to be mainly due to the stabilization of the radical and using the values of the ionization potential of the radical given in the table, we get the values in table 4 for the stabilization energies in the radical and its ion relative to the methyl radical.

As with paraffins, increasing the number of carbon atoms leads to an increase in the number of resonance structures, and increased branching leads to more of these structures becoming equivalent. The stabilization due to branching oes not seem to be greatly different for the molecule and its ion. The effects of the varying ionization potentials of the radicals on the unimolecular reactions of the alkyl halides have been discussed by Evans (7).

ALKYL DERIVATIVES OF H_2O, H_2S, NH_3, HCHO, AND THE HALOGEN ACIDS

Table 1 shows that the substitution of alkyl groups for hydrogen atoms produces large reductions in the ionization potentials in the classes of molecules which can be considered as the alkyl derivatives of water, hydrogen sulfide, ammonia, formaldehyde, and the halogen acids. The electrons concerned in these cases are the non-bonding electrons on the appropriate atoms (except for a minor difference in the case of nitrogen). It is clear that the amount of lowering of the ionization potential of RX relative to HX is greatly influenced by the electronegativity of the group X (R being the alkyl substituent). The contribution of hyperconjugation to the lowering of the ionization potential can probably be explained along the lines already indicated for propylene and the ethyl radical. It is necessary to consider the hyperconjugation between an alkyl group and an atom or group X with which are associated two or more π orbitals (usually non-bonding atomic orbitals) and to take some account of the effect of the electronegativities of X on the mixing coefficients in the molecular orbitals. With the exception of the alkyl derivatives of formaldehyde, the problems reduce to the three-center problem similar to that discussed for the ethyl radical. The centers are of course not equivalent, as they are for the allene radical discussed by Hückel. As a simplification we shall discuss the resonance interaction of the bonding and antibonding molecular orbitals of the alkyl group with the non-bonding X orbitals. The relative magnitudes of the interactions between these orbitals will depend on how close the energies (term values) of the non-bonding orbitals are to those of the bonding orbitals. In most cases they lie closer to the bonding than to the antibonding orbitals but at somewhat lower energies (i.e., less tightly bound) than the bonding orbitals themselves, so that the interaction elevates them to a greater extent than the interaction with the antibonding orbitals depresses them. This leads to a reduction in ionization potential for the non-bonding X electrons with an increase in the stabilization energy of the ion RX^+. Both these effects can be enhanced by a changing of the mixing coefficients as a result of the removal of the X electron and in this way lead to still further decrease in ionization potential.

TABLE 4

Stabilization of alkyl relative to methyl radical (ion) (in kilocalories per mole)

	ETHYL	*n*-PROPYL	ISOPROPYL	*n*-BUTYL	*tert*-BUTYL
Radical	2	4	7.5	5	9
Ion	34	56	60.5		76

Although it is only necessary to consider the relative changes of stabilization energy between RX and RX^+ to explain the reductions in ionization potential, it is important to have some idea of the *absolute* changes in the stabilization energy of the molecules as a result of alkyl substitution in order to appreciate the nature of the effects taking place. It is not so simple to find data which will indicate the stabilization of the molecule as a whole in passing from HX to CH_3X comparable, for example, to the way in which the heats of hydrogenation of ethylene and propylene indicate the stability of the latter with respect to the former. However, another method is available which will give some idea of the magnitude of this effect. Table 5 gives the heats of combustion at 25°C. of various classes of molecules in the gaseous state to give gaseous carbon dioxide and liquid water. If one takes the difference between the heats of combustion of two successive members of a straight-chain homologous series, then provided this is done for sufficiently high members, the value obtained will be 157.4 kcal. per mole. This can be taken as the contribution to the heat of combustion of a molecule by replacement of a hydrogen atom by a methyl group if there is little interaction of the methyl group with the rest of the molecule, i.e., no change in the resonance energy of the molecule. The difference between 157.4 and any increment observed can be taken as the stabilization energy resulting from the substitution, i.e.,

$$\text{Stabilization energy} = S = 157.4 - \{C\,(\text{RX}) - C\,(\text{HX})\}\ \text{kcal. per mole}$$

$\Delta_1 C$ is the increment when a primary hydrogen atom not forming part of a methyl group is replaced; $\Delta_2 C$ is the increment for replacing the hydrogen atom of a methyl group. Most of the values are taken from Wheland (41) and come originally from a table compiled by M. S. Kharasch and W. G. Brown; the remainder were obtained from Bichowsky and Rossini (3). S^+ is the change in stabilization energy of the ion as a result of substitution and is obtained by simply adding to S the change in ionization potential.

Let us consider first the alkyl derivatives of water. The introduction of the first methyl group produces destabilization. Presumably, the break-up of the fairly compact electronic structure which is possible in H_2O is responsible for this. Any stabilization by hyperconjugation between the methyl group and the non-bonding electrons of the oxygen atom is inadequate to counteract it. An effect which accompanies this and may be significant in its explanation is a reduction of the polarity of the bond to the oxygen—the moment of the carbon-oxygen bond is only 0.8 D as compared with 1.51 D for the oxygen–hydrogen bond. It is presumably possible for the oxygen to take an electron from a hydrogen atom and form a "neon-like" electronic structure more easily than it can do so with an electron in an orbital attached to an alkyl group. Following the initial destabilization there is a subsequent small increase in stability in going from methyl to ethyl and a still smaller one in going from ethyl to *n*-propyl. This is presumably associated with stabilization arising out of the increased polarizability of the alkyl group. In going from methyl alcohol to dimethyl ether, i.e., another primary replacement, there is destabilization, but it is not so great as that associated with the first replacement of hydrogen. Similar changes are observed to a lesser degree in the amines, and the same remarks about the moments of the nitrogen–hydrogen and nitrogen–carbon bonds can be made as for

TABLE 5

Heats of combustion, CH_2 *increments, and derived stabilization energies of various classes of molecules (in kilocalories per mole)*

SUBSTANCE	C	Δ_1C	Δ_2C	S	S^+
Water	10.5				
Methyl alcohol	182.6	172.1		−14.7	27.0
Ethyl alcohol	336.8		154.2	3.2	
n-Propyl alcohol	493.3		156.5	0.9	
Dimethyl ether	346.7	165.0		−7.6	− 0.7
Diethyl ether	660.3		156.3	1.1	
Ammonia	90.8				
Methylamine	256.9	166.1		−8.7	14.3
Ethylamine	413.1		156.2	1.2	
Dimethylamine	418.2	161.3		−3.9	0.7
Diethylamine	730.6		156.2	1.2	
Trimethylamine	579.5	161.3		−3.9	0.7
Triethylamine	*ca.* 1042.0		154.1		
Hydrogen sulfide	134.0				
Methyl mercaptan	297.6	163.6		−6.2	*ca.* 11.0
Ethyl mercaptan	452.0		154.4	3.0	
Dimethyl sulfide	455.6	158.0		−0.6	6.3
Hydrogen cyanide	159.0				
Methyl cyanide	310.4	151.4		6.0	*ca.* 29.0
Ethyl cyanide	464.6		154.2		
Acetylene	310.615				
Methylacetylene	463.109	152.594		4.8	**−2.5**
Ethylacetylene	620.86		157.75	−0.35	
1-Pentyne	788.08		157.17	0.23	
Dimethylacetylene	616.533	153.424		4.0	
2-Pentyne	774.33		157.8		
Ethylene	337.234				
Propylene	491.987	154.753		2.7	21.1
1-Butene	649.757		157.77	−0.37	0.6
1-Pentene	806.85		157.09	0.31	
trans-2-Butene	647.072	155.85		1.5	
trans-2-Pentene	804.26		157.19	0.21	
trans-2-Hexene	961.66		157.40	0.0	
Benzene	789.08				
Toluene	943.58	154.50		2.1	11.8
Ethylbenzene	1101.13		157.55	−0.15	
n-Propylbenzene	1258.24		157.11	0.29	
Hydrogen	68.3				
Methane	212.80	144.0		+13.0	66.0
Ethane	372.82	(160.0)	160.0	−2.5	32.0

TABLE 5—*Continued*

SUBSTANCE	C	Δ_1C	Δ_2C	S	S^+
Propane	530.605		157.785	−0.045	6.9
n-Butane	687.982		157.377	+0.023	
Formaldehyde	134.7				
Acetaldehyde	284.7	150.0		7.4	22.4
Acetone	434.6	149.9		7.5	10.5
Diethyl ketone	746.8		156.1		
Hydrogen chloride	12.1				
Methyl chloride	164.2	152.1		5.3	41.9
Ethyl chloride	316.7		152.5	4.9	13.2
Hydrogen bromide	25.54				
Methyl bromide	184.0	158.5		−1.1	18.9
Ethyl bromide	340.5		156.6	0.9	6.6
Hydrogen iodide	160.4				
Methyl iodide	200.5	160.4		−4.0	15.3
Ethyl iodide	357.8		157.3	0.1	3.4

those of the oxygen-hydrogen and oxygen–carbon bonds. The molecular ions in practically all cases are stabilized by substitution, the amount of stabilization being greater the greater the electronegativity of the central atom and considerably exceeding in magnitude the stabilizing or destabilizing effects which occur in the ground state.

When a methyl group replaces a hydrogen atom in acetylene, ethylene, benzene, hydrogen cyanide, or formaldehyde, stabilization occurs. This is largest when polar groups are involved, that is, in hydrogen cyanide and formaldehyde, indicating stability from charge transfer for these molecules in addition to simple hyperconjugation effects. The stabilization in methylacetylene is roughly twice that in propylene and toluene, in agreement with the two-dimensional character of the hyperconjugation for this molecule.

If one takes molecular hydrogen as the first member of the paraffins, then considerable stability is acquired in passing to the symmetrical molecule methane, an effect which is even more pronounced for the ion. This is, no doubt, to be associated with the great symmetry of the electronic structure of methane. In going to ethane this symmetry is lost, and the hyperconjugation stability which sets in is not adequate to offset the resulting destabilization.

The methyl derivative of hydrogen chloride has definite stabilization energy with respect to its parent, a fact which is contrary to what one might expect from analogy with the oxygen derivatives. Unfortunately, thermochemical data on the fluorine compounds is not available, but it is thought that for these compounds the analogy might be closer with oxygen derivatives, as there are possibilities of charge-transfer effects in heavier atoms which are not open to first-row atoms (i.e., possible use of 3*d* orbitals). Stabilization by two-dimensional hyperconjugation is of course possible for the alkyl halides. The molecular ions are stabilized greatly by methyl substitution, no doubt as a result of processes which lead to very considerable charge migration in the ion, which thus resonates between the forms R—X$^+$ and R$^+$—X. The lower the ionization potential of R, the greater this resonance would be expected to become, a conclusion which fits in with the lower ionization potentials for the isopropyl chlorides, *tert*-butyl chlorides, etc.

ABSORPTION SPECTRA

The long-wave-length shifts of absorption bands in general parallel the reductions in ionization potentials on alkyl substitution, though the wave-length shifts are of smaller magnitude because the excited state is not so strongly stabilized as the ionic state by hyperconjugation and charge transfer. Other effects are also present which sometimes give rise to small short-wave-length shifts. However, it is felt that only by considering separately the energy changes in the ground and in the excited states, as has been done here for the ionization potentials, will it be possible to get at the causes for some of the anomalous shifts observed. It is hoped that this principle will be carried over in a future paper dealing more specifically with absorption spectra, in particular the spectra of the substituted aromatics.

SUMMARY

The effect of alkyl substitution on the absorption spectra and ionization potentials of many classes of molecules is shown to be due mainly to preferential stabilization of the ionic or excited state. It is suggested that this is largely a result of hyperconjugation and charge transfer. Thermochemical and other data are used to support the arguments.

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