The Ionization and Dissociation of Methyl Butyl Ketones under Electron Impact.* I. Methyl *n*-Butyl Ketone and Methyl Isobutyl Ketone

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The method of equivalent orbitals has been applied by Hall and Lennard-Jones[1,2] to the calculation of the ionization potentials of normal paraffins; Fueki and Hirota[3] applied it to the predictions of the scission probability of each bond of normal paraffin positive ions, calculating the distribution of the positive charge over the molecular ion in the lowest ionized state. However, the order of the secular determinant which has to be solved in this method is too high for larger molecules to be solved without a computer. In the calculation of ionization potentials, Franklin[4] has simplified this problem by assuming that the molecular orbital can be set up from the united atom molecular orbitals, i.e., group orbitals, each of which represents a group of the molecule.

In the present research, calculations have been carried out in an attempt to predict the ionization potentials and the bond scission probabilities of methyl butyl ketones by assuming a wave function for each bond between the groups of the molecule. The results of the calculations have also been compared with those obtained from the mass spectra.

* A part of this paper was presented by M. Hatada and K. Hirota at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

1) G. G. Hall, *Proc. Roy. Soc.*, **A205**, 541 (1951).

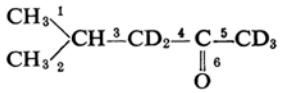
2) J. Lennard-Jones and G. G. Hall, *Trans. Faraday Soc.*, **48**, 581 (1952).

3) K. Fueki and K. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 212 (1960).

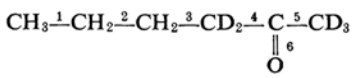
4) J. L. Franklin, *J. Chem. Phys.*, **32**, 1304 (1954).

Experimental

Materials.—Two types of methyl butyl ketone and their deuterated compounds, methyl isobutyl ketone (MIBK-d_0) and methyl *n*-butyl ketone (MNBK-d_0), were obtained from the Tokyo Kasei Co. and used after drying with drierite. Methyl isobutyl ketone-1,1,1,3,3-d_5 (MIBK-d_5) and methyl *n*-butyl ketone-1,1,1,3,3-d_5 (MNBK-d_5) were prepared from the ketones by repeated exchange with deuterium oxide, followed drying with drierite and distillation. Impurities of ca. 5% were found in the samples by gas chromatographic analysis. The isotopic impurities (d_4) of MIBK-d_5 and MNBK-d_5 were ca. 3 and 10% respectively.



(MIBK-d_5)



(MNBK-d_5)

The Measurement of Ionization Potentials and Mass Spectra.—The ionization potentials as well as the mass spectra of these compounds were obtained by the use of a Hitachi RMU-5 type mass spectrometer modified for the present purpose. The mass spectrometer is a 90° sector instrument. The accelerating potential was 1500 V., and magnetic scanning was employed. The ionization potentials were determined by the linear extrapolation method, calibrated with the first ionization potential of argon (15.75 eV.). The mass spectra were obtained using bombarding electrons of 90 eV.

Calculation

The secular equation for a molecule is:

$$|e_{ij}-\delta_{ij}E|=0$$

where i and j refer to various bonds between groups in the molecule, e_{ij} is the matrix element which shows the interaction between the group bond orbitals, ϕ_i and ϕ_j, and E is the energy of the molecular orbitals, the highest of which corresponds to the lowest ionization potential of the molecule. All interactions except those of adjacent group bonds are assumed to be zero. The secular determinant for methyl-isobutyl ketone is illustrated below:

$$\begin{vmatrix} e-E & b & b & 0 & 0 & 0 \\ b & e-E & b & 0 & 0 & 0 \\ b & b & e-E & b & 0 & 0 \\ 0 & 0 & b & e-E & b & c \\ 0 & 0 & 0 & b & e-E & c \\ 0 & 0 & 0 & c & c & f-E \end{vmatrix} = 0$$

The elements in the determinant are shown in Table I. The e and b elements were taken to be −13.75 eV. and −1.80 eV. respectively from the values obtained by Fueki[5] for saturated hydrocarbons. The elements c and f were calculated from the secular equations for acetone and methyl ethyl ketone using the measured ionization potentials of these two compounds. The values of c and f obtained in this way are −2.626 eV. and −12.37 eV. respectively.

TABLE I

	$C\underline{^{i}}C$	$C\underline{^{i+1}}C$	C-O
$C\underline{^{i}}C$	e	b	c
$C\underline{^{i+1}}C$	b	e	c
C-O	c	c	f

Results and Discussion

The calculated ionization potentials of MIBK and MNBK are shown in Table II, along with the measured ones. The square of the coefficient of the group bond orbital in the highest-occupied molecular orbital is shown in Table III as an indication of the distribution of the positive charge when an electron is removed from the molecule.

TABLE II

	Ionization potential eV.		
	Calcd.	Obs.	
Acetone	(9.92)[a]	9.73[b]	9.92[a]
Methyl ethyl ketone	(9.76)[a]	—	9.76[a]
Methyl isobutyl ketone-d_0	9.69[b]	9.33[b]	
Methyl isobutyl ketone-d_5	9.69[b]	9.35[b]	
Methyl *n*-butyl ketone-d_0	9.70[b]	9.77[b]	9.71[a]

a) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).
b) This work.

The mass spectra of MIBK, MNBK and their deuterated compounds are shown in Fig. 1. The peaks which appear in the mass spectra of MIBK can be classified into (C_1), (C_2, CO), (C_2O, C_3), (C_4), (C_3O), (C_5O) and (C_6O) groups. The sum of the relative intensities of the peaks in each group in the mass spectra of the d_0 compound was nearly equal to the corresponding one, as they were in those of d_5.

The peak of d_0, at $m/e=43$ which was the highest, shifted to 46 in the mass spectrum of d_5. Thus, this ion has been assigned to $\underline{CH_3}CO^+$, which is formed by the scission of bond 4.* Since the peak of d_0 at $m/e=57$ shifted to $m/e=59$, this ion is probably $(CH_3)_2CH\text{-}\underline{CH_2}^+$. The peak of d_0 at $m/e=58$ shifted to $m/e=63$ upon deuteration. This

5) K. Fueki, *J. Phys., Chem.*, **68**, 2856 (1964).
* The hydrogen atom exchangeable by the exchange reaction with D_2O is shown by $\underline{H}$.

TABLE III

		1	2	3	4	5	6
MIBK							
c_i^2%	($\sum_{i=1}^{6} c_i^2 = 100$)	0.89	0.89	9.45	25.45	6.88	56.44
c_i^2%	($\sum_{i=1}^{5} c_i^2 = 100$)	2.3	2.3	21.7	58.4	15.8	—
MNBK							
c_i^2%	($\sum_{i=1}^{6} c_i^2 = 100$)	0.53	2.66	8.68	26.96	6.97	56.21
c_i^2%	($\sum_{i=1}^{5} c_i^2 = 100$)	1.2	6.1	19.8	57.4	15.9	—

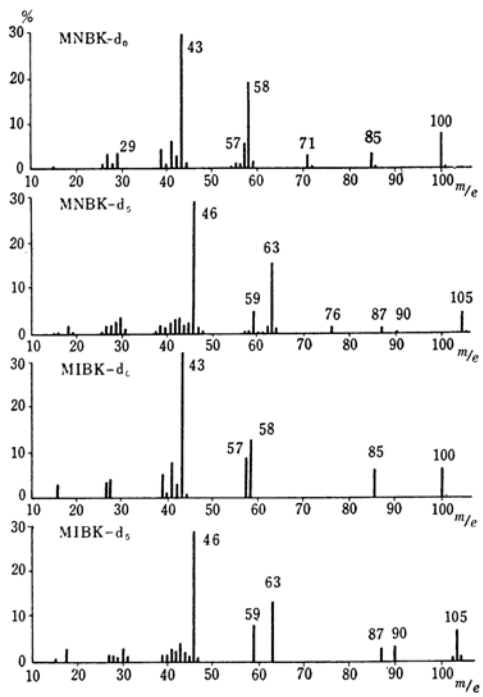


Fig. 1. Mass spectra of MNBK-d_0, MNBK-d_0, MIBK-d_5 and MIBK-d_5. Per cent. of total ionization vs. m/e.

ion is interpreted as $\underline{CH_3}COC\underline{H_2}H^+$ formed by the following hydrogen transfer reaction:

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\rangle CH\text{-}C\underline{H_2}\text{-}COC\underline{H_3} \longrightarrow$$

$$C\underline{H_3}COC\underline{H_2}H^+ + CH_3CH{=}CH_2 + e$$

This reaction was also found by Ausloos[6] in the ionization and dissociation of methyl-*n*-propylketone-1, 1, 1, 3, 3-d_5. Since the peak of d_0 at $m/e=85$ splits into peaks of $m/e=87$ and 90 upon deuteration, this peak is interpreted as consisting of two ions which have the same mass, $\overset{+}{C}O\text{-}CH_2\text{-}C\underline{H}(CH_3)_2$. and $C\underline{H_3}CO\text{-}C\underline{H_2}\text{-}\overset{+}{C}H\text{-}CH_3$. Similar results are also obtained in the cases of MNBK-d_0 and -d_5.

6) P. Ausloos and E. Murad, *J. Am. Chem. Soc.*, **80**, 5929 (1958).

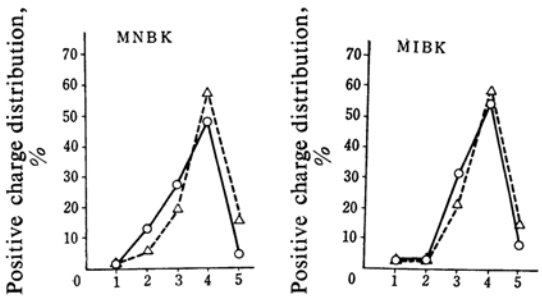


Fig. 2. Bond scission probability and positive charge distribution in MNBK and MIBK.
—○— Experimental: probability of bond scission
--△-- Theoretical: positive charge distribution

Figure 2 shows the relation between the bond scission probability and the position at which the bond scission occurs. The scission at bond 6 was excluded from the calculations, because the removal of an electron from the C=O bond was considered not to cause the scission of this bond and, actually, no scission at this bond was found in the mass spectra. Figure 2 illustrates that a close correlation exists between the measured and calculated values for MIBK and MNBK.

This paper has not described anything about the C-H bond scission, which seems to be related to the $CH_3COC\underline{H_2}H^+$ formation which involves the hydrogen transfer reaction. This is a problem which will require further study.

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