

### Stability of Ethylidene Radicals

G. B. KISTIAKOWSKY AND BRUCE H. MAHAN  
Gibbs Chemical Laboratory, Harvard University,  
Cambridge, Massachusetts  
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PREVIOUS attempts to study the ethylidene radical have involved the photolytic and thermal decomposition of diazoethane,  $\text{CH}_3\text{CHN}_2$ .<sup>1-4</sup> The radical may also occur as an intermediate in the reactions of Na atoms with the asymmetrical dihalides of ethane,<sup>5,6</sup> as well as in the photolysis and pyrolysis of acetaldazine,  $\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$ .<sup>1,7</sup> We report here evidence for the existence of ethylidene in the photolysis of methyl ketene,  $\text{CH}_3\text{CHCO}$ .

Methyl ketene was prepared by the method of Jenkins,<sup>8</sup> and purified by a slow bulb-to-bulb distillation, discarding the first and last quarters of the distillate. A typical preparation was 99.9% absorbed by ascarite.

Photolyses were carried out in a Pyrex cell at  $24^\circ\text{C} \pm 2^\circ\text{C}$ , using a high-intensity, low-pressure mercury arc. The effective radiation was therefore confined to the 3130 Å, 3340 Å, and 3650 Å wavelengths. By confining the investigation to pressures less than 40 mm Hg of methyl ketene, corrections for the dark reaction (dimerization of methyl ketene) were kept small or unnecessary. The course of the reaction was followed manometrically using a quartz spiral manometer, and the products were analyzed in a gas analytical system similar to the one described by Nash.<sup>9</sup> Combustion over CuO showed the non-condensable fraction of the photolytic products to be CO. The condensable fraction could be further separated into two sub-fractions, one condensable in boiling  $\text{CH}_4$ , ( $-161^\circ\text{C}$ ) the other noncondensable. Hydrogenation of this latter subfraction showed it to be a mono-olefin, and its infrared spectrum showed the 10.52 micron Q-branch absorption of ethylene. The higher boiling subfraction was also shown to be a mono-olefin by hydrogenation, and upon combustion proved to be a  $\text{C}_4$  compound. The amount of this fraction collected so far is so small as to preclude identification by infrared analysis, but it may be assumed to be a mixture of the butenes.

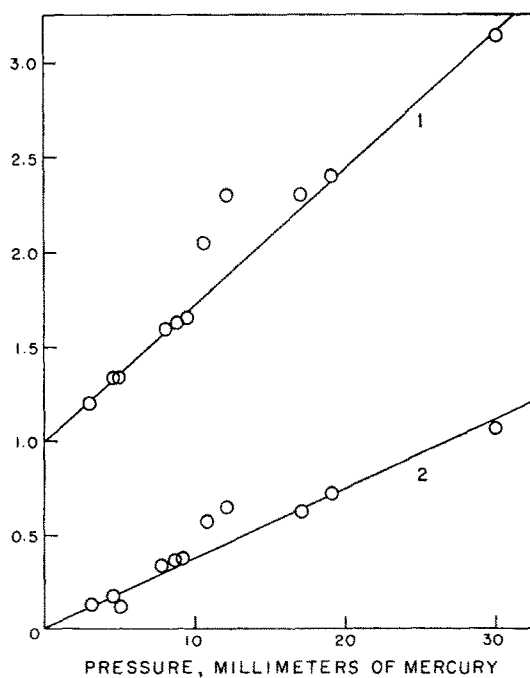
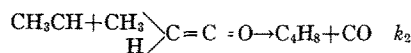
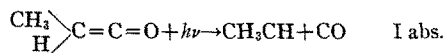


FIG. 1. Relative rates of production of three products as a function of methyl ketene pressure. Line 1 and experimental points show the ratio  $\text{CO}/\text{C}_2\text{H}_4$ , line 2 and points, the ratio  $\text{C}_4\text{H}_8/\text{C}_2\text{H}_4$ .

During the photolysis of pure methyl ketene, the pressure increased linearly with time up to about 15% decomposition. Beyond this point the slope decreased continuously, indicating an inhibitory action by one of the products. Addition of ethylene to the methyl ketene decreased the slope of the pressure-time curve (i.e., the manometric rate), indicating that it might be responsible for the effect observed at large percentage decomposition.

Measurements of the initial rate of production of CO,  $\text{C}_2\text{H}_4$ , and  $\text{C}_4\text{H}_8$  as a function of initial pressure of methyl ketene were made. As seen in the Fig. 1, a plot of the  $\text{CO}/\text{C}_2\text{H}_4$  ratio as a function of initial methyl ketene pressure is a straight line with unit intercept. Similarly, a plot of the  $\text{C}_4\text{H}_8/\text{C}_2\text{H}_4$  ratio as a function of the initial pressure is linear with a zero intercept. These data strongly suggest the following mechanism:



A steady-state treatment yields for the ratio of the rate of CO production to  $\text{C}_2\text{H}_4$  production  $\text{CO}/\text{C}_2\text{H}_4 = 1 + 2k_2P/k_1$ , and for the rate of  $\text{C}_4\text{H}_8$  production relative to  $\text{C}_2\text{H}_4$  production  $\text{C}_4\text{H}_8/\text{C}_2\text{H}_4 = k_2P/k_1$ . Thus we see that under the conditions of our experiments the rate of rearrangement of the ethylidene radical to ethylene is comparable to the rate of attack of ethylidene on methyl ketene.

The effects of temperature, inert gas, light intensity, and wavelength are being investigated and will be reported later.

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### Structure of Feather Keratin\*

S. KRIMM AND R. SCHOR  
Harrison M. Randall Laboratory of Physics, University of Michigan,  
Ann Arbor, Michigan  
(Received February 10, 1956)

NO completely satisfactory structure has as yet been proposed for the rachis of feather. Early x-ray diffraction studies<sup>1</sup> were thought to indicate that the component polypeptide chains were essentially in the extended, or  $\beta$ , configuration. This conclusion was based on the observation<sup>2</sup> that, although the characteristic 3.08 Å meridian spacing is smaller than the spacing usually found in the  $\beta$  proteins (*viz.*, 3.3 to 3.5 Å), it could be increased almost to the required value by stretching the specimen. Recent studies on the structure of proteins, however, have yielded the suggestion<sup>3,4</sup> that the  $\alpha$  helix<sup>5</sup> may be a component part of the structure. No definite experimental evidence has as yet been presented which would permit an unambiguous choice between these two possibilities. We discuss here some calculations which bear on this point, and also present a tentative model for the structure of this protein.

As a preliminary to the calculation of the cylindrical Patterson function<sup>6</sup> for feather keratin, we have calculated the one-dimensional Patterson projection,  $P(r)$ . This gives the density of interatomic vectors whose radial component is  $r$ . In this calculated  $P(r)$ , maxima occur at about  $r=5$  Å and  $r=10$  Å, there being a minimum near  $r=3$  Å. It is pertinent to compare this with the  $P(r)$  which is to be expected for an  $\alpha$  helix. The characteristic feature of this  $P(r)$  is found<sup>7</sup> to be a first maximum at about  $r=3$  Å. This comparison suggests that  $\alpha$  helices with their axes parallel to the fiber axis are not a component part of the structure.

Rather, in view of the observed maxima in  $P(r)$ , it appears most likely that the structure is based on extended polypeptide chains.

The model which we propose for the structure of feather keratin has the following features: (1) The fundamental unit is a helical extended polypeptide chain of pitch 190 Å and radius 8.0 Å. There are 64 amino acid residues in the 190 Å repeat. (2) In the 190 Å repeat there are 8 uniformly spaced proline residues. (3) Ten of these helices aggregate coaxially as a result of lateral hydrogen bonding between chains, the proline residues of neighboring chains packing together at about the same level. The polypeptide chains are in the parallel configuration<sup>8</sup> and are about 4.85 Å apart. The side chains project both into and out of the approximately cylindrical unit formed by the main chains. (4) Seven of these cylindrical units form a somewhat stable aggregate.

The percentage of proline required by the proposed model is in good agreement with that found.<sup>9</sup> The model accounts fairly well for the strong equatorial and meridian reflections in the x-ray diffraction pattern, and in particular for the stable<sup>10</sup> meridian reflection at 23.7 Å, which arises from the axial repeat of the proline residues. Fair agreement with the equatorial intensities is obtained with the assumed packing arrangement. The agreement is improved if it is assumed that the hole through the center of the cylindrical unit contains water. The structure predicts an infrared dichroism which is consistent with the observed value.<sup>11</sup> Construction of molecular models, with particular reference to the configuration of the polypeptide chain near the proline residue, indicates that the proposed structure is a most likely one. The relatively homogeneous particles which are obtained when feather keratin is solubilized<sup>12,13</sup> can be accounted for by the susceptibility to hydrolysis of certain of the peptide links adjacent to the proline residues.<sup>14</sup> The apparent absence of end groups in soluble feather keratin<sup>15</sup> is probably a consequence of the inadequacy of the dinitrofluorobenzene method when the terminal group is proline.<sup>16,17</sup>

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## Linear Extrapolation of the Vibrational Energy Levels of Ionic Molecules

CHARLES L. BECKEL

Department of Physics, Georgetown University, Washington, D. C.

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IN a comparison of the true values of the dissociation energies  $D_0$  of diatomic molecules with those values obtained through linear extrapolation of vibrational energy levels,  $D_{lin}$ , Gaydon<sup>1</sup> found  $D_0 < D_{lin}$  for the ground electronic states of all non-ionically bound molecules except  $Cl_2$  and  $CIF$ . The recent  $CIF$  data of Nielsen and Jones<sup>2</sup> yielded a ratio  $D_0/D_{lin}=0.86$ , and further strengthened the conviction that  $D_0 < D_{lin}$  for all non-ionic molecules. Gaydon's comparison of  $D_0$  and  $D_{lin}$  for predominantly ionic molecules led to no such uniformity. In the case of ionic molecules it was expected that  $D_0 > D_{lin}$ , and this was true for only six of the ten molecules with sufficient data for a comparison.

TABLE I.  $D_i/D_{lin}$  for the halides of Al, Ga, In, and Tl.

Molecule	Vibrational data reference	$D_{lin}$ (in ev)	$D_0$ (in ev)	$D_i$ (in ev)	$D_i/D_{lin}$
AlF	a	4.2	6.7	9.1	2.2
AlCl	b	3.7	5.1	7.3	2.0
AlBr	b	3.4	4.3	6.8	2.0
AlI	b	3.1	3.9	6.7	2.2
GaF	c	3.5	6.2	8.6	2.5
GaCl	d	3.1	5.0	7.2	2.3
GaBr	b	2.6	3.5	6.0	2.3
GaI	b	2.9	2.9	5.7	2.0
InF	e	3.3	5.4	7.6	2.3
InCl	b	3.1	4.5	6.5	2.1
InBr	b	2.3	3.4	5.7	2.5
InI	b	2.4	2.8	5.4	2.3
TlF	b	3.7	4.8	7.3	2.0
TlCl	b	2.0	3.8	6.1	3.1
TlBr	b	2.9	3.2	5.8	2.0
TlI	f	5.3	2.6	5.5	1.04

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It is the purpose of this letter to present the results of a re-examination, through the use of data recently available, of the values of  $D_{lin}$  for ionic molecules.

The re-examination was in the form of a comparison of  $D_{lin}$  with  $D_i = D_0 + I - E$ , where  $D_i$  is the dissociation energy of the molecule into ions,  $I$  is the ionization energy of the metallic atom, and  $E$  is the electron affinity of the nonmetallic atom.  $D_{lin}$  was compared with  $D_i$  rather than with  $D_0$ , since near equilibrium the vibrational energy levels are those of a molecule which dissociates into ions rather than into atoms. The values of  $D_0$ ,  $I$ , and  $E$  were taken from Gaydon,<sup>3</sup> Herzberg<sup>4</sup> and Pritchard,<sup>5</sup> respectively.  $D_{lin}$  was found from the empirical values of the spectroscopic constants  $\omega_e$  and  $\omega_e x_e$  through use of  $D_{lin} = \omega_e^2 / 4\omega_e x_e - \frac{1}{2}\omega_e$ .

In Table I the values of  $D_i/D_{lin}$  are shown for the halides of Al, Ga, In, and Tl. These metals have low ionization energies, and with the halogens form molecules which, in all likelihood, are predominantly ionic. It can be seen that in every case  $D_i > D_{lin}$  and, in fact, except for TlCl and TlI, all values of  $D_i/D_{lin}$  are reasonably close to 2.25. It might be noted that for TlCl Miescher's<sup>12</sup> vibrational analysis leads to  $D_i/D_{lin} = 2.0$ . The vibrational analysis for TlI, while recently revised, still seems open to criticism.

Tables II and III compare  $D_i$  and  $D_{lin}$  for the most ionic molecules, the alkali halides. At present, these comparisons cannot be as meaningful as comparisons for the molecules listed in Table I, because the electronic transitions from which the values of  $D_{lin}$  are obtained lead to bands rather than sharp lines. Moreover, pure vibrational transitions have never been analyzed for an alkali halide molecule.

The values of  $D_{lin}$  in Table II are based on the analyses of Levi.<sup>13</sup> While considerable fluctuation in the value of  $D_i/D_{lin}$  occurs, in every case the ratio  $> 1$ .

TABLE II.  $D_i/D_{lin}$  for the alkali halides studied by Levi.<sup>a</sup>

Molecule	$D_{lin}$ (in ev)	$D_0$ (in ev)	$D_i$ (in ev)	$D_i/D_{lin}$
LiI	4.2	3.5	5.7	1.4
NaCl	4.5	4.2	5.5	1.2
NaBr	2.7	3.8	5.4	2.0
NaI	3.4	3.1	5.0	1.5
KCl	2.7	4.4	4.9	1.8
KBr	2.3	3.9	4.7	2.0
KI	2.0	3.3	4.4	2.2

<sup>a</sup> See reference 13.