457. *The Electronic Spectrum of Formaldehyde. Part II.* Mechanisms of Dissociation of Formaldehyde and the Formaldehyde Molecular Ion.*

By J. C. D. Brand and R. I. Reed.

Predissociation in the $^1A''$ state of formaldehyde is discussed in terms of the value D(H–CHO) = 75·1 kcal. mole^{-1} recently obtained by electron-impact measurements.[1] In addition to the strong predissociation at 2850 Å, a second region of weak predissociation is identified at long wavelengths (~3500 Å) which strongly supports a low value for the dissociation energy of formaldehyde.

The assignment of low-lying states of formaldehyde and formyl molecular ions (CH_2O^+ and CHO^+) is considered and a set of reasonable (though not uniquely determined) adiabatic correlations is drawn for the separated states of H + CHO^+, H^+ + CHO, H + CO^+, etc. The results emphasise that decomposition of ions in the mass-spectrometer, in cases when the product is formed without excess of kinetic energy, almost certainly involves a radiationless transition.

The dissociation energy of formaldehyde has been discussed in many papers. Kinetic evidence [2] from the photolysis of formaldehyde [3,4] and acetaldehyde [5] supports a value for D(H–CHO) of 89—91 kcal. mole^{-1} which must represent an upper limit as in these experiments decomposition is commonly initiated at 3130 Å (91·3 kcal. mole^{-1}). The isotopic-tracer method [6] favours a much lower photochemical threshold, near 3650 Å, from which it has been argued that D(H–CHO) does not exceed 78 kcal. mole^{-1}. Electron-impact measurements with formaldehyde [1] (together with a thermochemical cycle) furnish the lowest value of all, D(H–CHO) = 75·1 ± 2·3 kcal. mole^{-1}, and this determination is the basis of the present discussion. It will be shown that a low value of D(H–CHO) offers a promising explanation of hitherto unexplained aspects of the electronic spectrum of formaldehyde.

The ionisation efficiency curves for formaldehyde have well-defined breaks, at energies greater than the appearance potential, which are assigned to excited electronic states of the molecular ions CH_2O^+ and CHO^+. The mechanism of dissociation is discussed in the following sections.

EXPERIMENTAL

Electron-impact measurements were made with a Metropolitan-Vickers M.S.2 spectrometer. The experimental procedure and instrumental modifications have been described previously.[1] Appearance potentials were located (within ± ~0·1 v) by the method of extrapolated voltage differences,[7] and higher breaks (±0·2—0·3 v) by the method of linear intercepts.[8] The energy distribution in the electron beam (analogue of optical slit width) restricted the resolving power of the spectrometer to *ca.* 0·3 v.

Results.—The appearance potentials and higher breaks in the ion-current curves for CH_2O^+, CHO^+, and the corresponding deuterated ions are listed in Table 1, values obtained by Price and Sugden [9] in an ionisation tube (without mass resolution) being entered for comparison. The inflection at 12·2 v (CH_2O^+) was identified at higher gas pressures only but is considered to be

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* Part I, *J.*, 1956, 858.

[1] Reed, *Trans. Faraday Soc.*, 1956, **52**, 1195.

[2] Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, 1954, Chap. V.

[3] Calvert and Steacie, *J. Chem. Phys.*, 1951, **19**, 176.

[4] Horner, Style, and Summers, *Trans. Faraday Soc.*, 1954, **50**, 1201.

[5] Calvert, Pitts, and Thompson, *J. Amer. Chem. Soc.*, 1956, **78**, 4239.

[6] Klein and Schoen, *J. Chem. Phys.*, 1956, **24**, 1094.

[7] Warren, *Nature*, 1950, **165**, 810.

[8] McDowell and Warren, *Discuss. Faraday Soc.*, 1951, **10**, 55.

[9] Sugden and Price, *Trans. Faraday Soc.*, 1948, **44**, 116.

real and to correspond to the 11·8 v break recorded by Price and Sugden: their inflection at 13·1 v may correspond to *A* (CHO^+), to the 13·3—13·6 v break (CH_2O^+) observed by us, or to an unresolved mixture thereof.

The particle of mass 31 in the spectrum of CH_2O is too abundant to be assigned to [$^{13}C_1$]-formaldehyde. Its appearance potential is so close to *I* (CH_2O) that it must be formed from CH_2O^+ ions by a hydrogen-transfer reaction,[10] $CH_2O^+ + H{\cdot}CHO = CH_2{\cdot}OH^+ + CHO$.

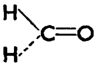
A search was also made for diffuse peaks, due to metastable ions having a low probability of dissociation or predissociation:[11] metastable D_2CO^+, HCO^+, and DCO^+ ions would occur at apparent mass-numbers (28·1, 27·1, and 27·4, respectively) which are resolved by the instrument; but none was observed.

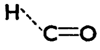
TABLE 1.

	CH_2O^+					CO^+	
$CH_2{\cdot}OH^+$	Sudgen & Price [9]		CD_2O^+	CHO^+	CDO^+	from CH_2O	from CD_2O
10·87 ± 0·2	(10·82)	10·87 ± 0·07	10·88 ± 0·08	—	—	—	—
	11·8 ± 0·2	(12·2 ± 0·2)	—	—	—	—	—
	13·1 ± 0·2	13·6 ± 0·2	13·3 ± 0·2	13·10 ± 0·08	13·10 ± 0·12	—	—
	—	—	—	18·4 ± 0·3	18·8 ± 0·3	18·7 ± 0·2	18·8 ± 0·3

DISCUSSION

(1) *Correlation Rules.*—In the following we are concerned mainly with the decomposition of a tetratomic molecule into an atom and a triatomic molecule (*e.g.*, $CH_2O = H + CHO$), or of a triatomic molecule into an atom and a diatomic molecule. The restrictions imposed by symmetry on the permitted states of the product are governed by the symmetry elements common to the reactant, transition state, and products, and their application is subjective in that the symmetry of the transition state cannot be determined by experiment. It will be assumed that planar states of CH_2O and CH_2O^+ and non-linear states of CHO dissociate through a planar transition state (C_s), (I) or (II); and that linear states of CHO or CHO^+ dissociate through a linear transition state ($C_{\infty v}$). The form of the correlation rules is the same for ions and uncharged molecules. Because the excitation energy of H and H^+ is large we need consider only those rules[12] which relate to S_g atomic states (Table 2 and 3). However, there is the further possibility[2] of molecular decomposition of the type, $H_2CO = H_2 + CO$, presumably by way of a C_{2v} transition state (III), and the rules for this case are given in Table 4. In addition to the permitted orbital correlations the same multiplicity rules hold as for diatomic molecules.[13]


(I)


(II)

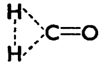

(III)

TABLE 2. *Correlation rules for the reaction* $H_2CO = H + HCO$. In the decomposition of a pyramidal (C_s) state of formaldehyde the transition state (C_1) has no symmetry element and all correlations are permitted subject to the multiplicity rules.

Species B_2 and B_1 are defined as, respectively, *s* and *a* to the molecular plane, σ_{yz}, of a C_{2v} formaldehyde. This is the reverse of the convention adopted in Part I. The resolution of the species of C_{2v} into those of C_s is contained in the first two columns of the Table.

Reactant	Transition state	Atom + triatomic molecule	
C_{2v}	C_s	$C_{\infty v}$	C_s
A_1, B_2	A'	$S_g + \Sigma^+, \pi, \Delta \ldots$	or A'
A_2, B_1	A''	$S_g + \Sigma^-, \pi, \Delta \ldots$	or A''

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[10] Norton, Nat. Bur. Stand. Circ. 522, p. 201.

[11] Hipple, Fox, and Condon, *Phys. Rev.*, 1946, **69**, 347.

[12] Shuler, *J. Chem. Phys.*, 1953, **21**, 624.

[13] Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York, 1950, p. 319.

TABLE 3. *Correlation rules for the dissociation of linear states of* HCO^+. Atomic states other than S_g are not considered here. The correlation rules for the dissociation of non-linear states can be read from the second and the final column of Table 2.

Products →

Atom ↓ \ $C_{\infty v}$	Σ^+	Σ^-	π	Δ	..
	Reactant				
S_g	Σ^+	Σ^-	π	Δ	..

TABLE 4. *Correlation rules for molecular dissociation,* $H_2CO = H_2 + CO$.

Products →

CO ↓ \ H_2	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	$\pi_g, \Delta_u . . .,$	$\pi_u, \Delta_g . . .$
			Reactant (C_{2v})			
Σ^+	A_1	B_2	B_1	A_2	$A_2 + B_2$	$A_1 + B_1$
Σ^-	A_2	B_1	B_2	A_1	$A_1 + B_1$	$A_2 + B_2$
π	$B_1 + B_2$	$A_1 + A_2$	$A_1 + A_2$	$B_1 + B_2$	$A_1 + A_2 + B_1 + B_2$	
Δ	$A_1 + A_2$	$B_1 + B_2$	$B_1 + B_2$	$A_1 + A_2$	,,	
...	...	...	...	...	...	

In constructing correlation curves for the electronic states of reactants and products it will be recalled that the crossing of states of the same symmetry species is not forbidden for more-than-diatomic molecules.[14] Subject to the Franck–Condon principle, radiationless transitions between electronic states of the same symmetry (equivalent to homogeneous perturbations of the states of diatomic molecules) may have high probability in the critical region of a crossing, and radiationless transitions between states of different symmetry may be permitted when vibrational-electronic interaction is taken into account.[15] The rules in Table 2—4 apply therefore to vibronic states as well as to purely electronic states. Symmetry considerations place relatively few restrictions on the permitted states of the products of an adiabatic decomposition.

In Table 5 are listed the heats of formation of the separated states of H + HCO, H^+ + HCO, H + CO^+, etc., which require consideration in drawing up sections of the electronic term manifold of H_2CO, H_2CO^+, and HCO^+. References to the thermochemical and spectroscopic sources are given in the Appendix.

TABLE 5.

Reactant	Separated states of product	Multiplicity	Energy relative to CH_2O ($^1A_1$) (kcal. mole^{-1})	(ev)
HCO^+	$H^+(^1S_g) + CO(^1\Sigma^+)$	1	367	15·91
	$H(^2S_g) + CO^+(^2\Sigma^+)$	1, 3	376	16·32
	$H(^2S_g) + CO^+(^2\pi_i)$	1, 3	435	18·89
H_2CO	$H_2(^1\Sigma_g^+) + CO(^1\Sigma^+)$	1	1·3	0·05
	$H(^2S_g) + HCO(^2A'')$	1, 3	75·1	3·26
	$H(^2S_g) + HCO(^2\Sigma^+)$	1, 3	99·4	4·31
	$2H(^2S_g) + CO(^1\Sigma^+)$	1, 3	105	4·58
H_2CO^+	$H(^2S_g) + HCO^+(^1\Sigma^+)$	2	303	13·13
	$H_2(^1\Sigma_g^+) + CO^+(^2\Sigma^+)$	2	324	14·06
	$H_2^+(^2\Sigma_g^+) + CO(^1\Sigma^+)$	2	357	15·48
	$H^+(^1S_g) + HCO(^2A'')$	2	388	16·86
	$H^+(^1S_g) + HCO(^2\Sigma^+)$	2	413	17·91
	$H^+(^1S_g) + H(^2S_g) + CO(^1\Sigma^+)$	2	418	18·17
	$2H(^2S_g) + CO(^2\Sigma^+)$	2, 2, 4	428	18·58

(2) *Predissociation of Formaldehyde.*—According to the electron-impact measurement,[1] D(H–CHO) = 75·1 kcal., the ground state of CHO is lower in energy than the first excited

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[14] Teller, *J. Phys. Chem.*, 1937, **41**, 109.

[15] Sponer and Teller, *Rev. Mod. Phys.*, **1941**, **13**, **76**.

singlet state of formaldehyde (28,198 cm.$^{-1}$ = 80·6 kcal. mole^{-1}) (Part I). The possibility exists, therefore, of predissociation covering the whole band system which, in regard to absorption from the vibrationless ground state, stretches from 3550 to below 2500 Å; this is consistent with the photolysis studies,[6] but in the present section we shall be concerned with purely spectral evidence. It is well known that the absorption is diffuse at wavelengths less than ~2850 Å [16, 17] but at the long-wavelength end of the spectrum the rotational line-width (*ca.* 0·1 cm.$^{-1}$) [19] does not exceed the Döppler broadening and the probability of dissociation must be quite small.

The evidence for predissociation near the zero-point level of the excited state is twofold: the impurity of the electronic wave function and the inactivity in emission of low-lying vibrational levels. Fig. 1 represents the levels of the zeroth and first quanta of the wagging vibration, $\nu_4(\omega CH_2)a'$, of the $^{1}A''$ (C_s) excited state, each level being split into inversion doublets by the non-planar geometry of the nuclei. The levels active in fluorescence are those in Fig. 1, plus combinations with one or two quanta of $\nu_3(\nu CO)a'$; the number of bands recorded (Part I) from each of the emitting levels is given in Table 6.

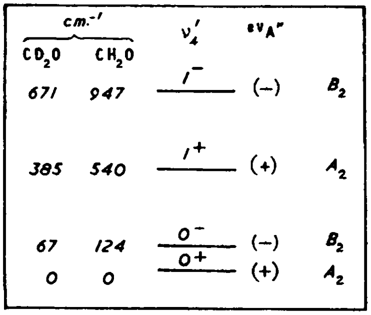

FIG. 1. *Low-lying A'' vibronic states of excited formaldehyde. In addition to the C_s symmetry of the nuclei, the potential field has C_2 symmetry on account of the inversion doubling and the +, − classification defines the character of the wave-functions under the operations of the groups C_2. Equivalent species of a C_{2v} formaldehyde are given on the extreme right.*

TABLE 6.

		$[^1H_2]$Formaldehyde		$[^2H_2]$Formaldehyde	
ν_4	ν_3	Height (cm.$^{-1}$)	No. of bands in emission	Height (cm.$^{-1}$)	No. of bands in emission
0$^+$	0	0	6	0	18
0$^-$	0	124	7	67	15
1$^+$	0	540	—	385	5
1$^-$	0	947	—	671	2
0$^+$	1	1171	3	1178	2
0$^-$	1	1308	1	1243	2
1$^+$	1	2150	—	1559	1
0$^+$	2	2323	1	2336	1

In the present paper the notation for the fundamental vibrational modes follows the recommendation of the recent Report (*J. Chem. Phys.*, 1955, **23**, 1997). The symbols for the totally symmetrical modes of excited ($^{1}A''$) formaldehyde are summarised below.

		Frequency (cm.$^{-1}$)				Frequency (cm.$^{-1}$)	
This paper	Part I	CH$_2$O	CD$_2$O	This paper	Part I	CH$_2$O	CD$_2$O
$\nu_1(\nu CH)a'$	ν(CH)	2875	2078	$\nu_3(\nu CO)a'$	ν(CO)	1182	1176
$\nu_2(\delta CH_2)a'$	δ(CH$_2$)	1322	989	$\nu_4(\omega CH_2)a'$	γ(CH$_2$)	682	494

It will be seen that no transitions are observed from the levels $\nu_4 = 1^+, 1^-$ of $[^1H_2]$formaldehyde * although they are present in approximately the expected abundance in the

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* The existence of the 1$^+$ level has been queried because of its inactivity in fluorescence: [19a] this objection lacks appreciation of the fact that at least five transitions are recorded from this level in the spectrum of $[^2H_2]$formaldehyde.

[16] Schou, *J. Chim. phys.*, 1928, **25**, 655; 1929, **26**, 1.

[17] Herzberg, *Trans. Faraday Soc.*, 1931, **27**, 378.

[18] Dieke and Kistiakowsky, *Phys. Rev.*, 1934, **45**, 4.

[19] Robinson, (*a*) *Canad. J. Phys.*, 1956, **34**, 699; (*b*) *J. Chem. Phys.*, 1954, **22**, 1384.

spectrum of [$^2H_2$]formaldehyde. The possibility that the excitation fails to populate the 1^+ and 1^- levels seems remote. Excitation has usually been in an electric discharge but the conditions [19b, 20] vary considerably from those in Part I and in no case has emission been reported from the 1^+ and 1^- vibrational states; moreover, if the excitation were responsible, it should be selective for both [$^1H_2$]- and [$^2H_2$]-formaldehyde. We conclude that the " missing " levels indicate a predissociation which sets as an upper limit $D(\text{H–CHO}) \leqslant 28{,}736$ cm.$^{-1}$ (82·3 kcal. mole^{-1}).

The second relevant observation is that the vibrationless ground state of formaldehyde combines in absorption with the $\nu_4(\omega CH_2)a' = 0^+$, 1^+ levels of the $^eA''$ state and with combinations of them with $\nu_2(\delta CH_2)a'$ and $\nu_3(\nu CO)a'$ (Part I). The transitions are of type A, and of very low intensity compared with the main absorption bands (which are of type B), but they are present in the spectra of [$^1H_2$]-, [$^2H_1$]-, and [$^2H_2$]-formaldehyde and their assignment is non-equivocal. These type A bands are allowed by the overall selection rules but are forbidden by the asymmetric top rules: vibronically, they are $A_1 \longleftrightarrow A_2$ transitions in the C_{2v} notation (Fig. 1). The breakdown of the asymmetric top rules must be due to the approximation implicit in the factorisation of the overall gyrovibronic wavefunction,

$$\psi_{evr} = \psi_e\psi_v\psi_r$$

of the excited state, and this in turn indicates a perturbation operating on the ψ_e function of the excited state. Specifically the observation of the type A transitions means that the $^eA''$ upper state has some $^eA'$ character, the presence of the type A bands being then analogous to the " extra-lines " in diatomic molecule spectra. It is natural to assume that the perturbing $^eA'$ state is associated with the predissociation of the $^eA''$ state discussed above, and therefore that the predissociation involves an $A'' \longrightarrow A'$ radiationless transition to a dissociative A' state. The radiationless transition must have a very low probability, for it is sufficient to interrupt emission only from excited vibrational states of ν_4: and, conversely, the probability must increase with increasing amplitude of ν_4. As the turning points of the vibration are symmetrically placed on each side of the inversion plane of the $^eA''$ state we conclude that the perturbing $^eA'$ state is strongly pyramidal, and the smaller efficiency of predissociation from $\nu_4 = 1$ levels of [$^2H_2$]formaldehyde can then be understood in terms of the smaller vibrational amplitude.

The lowest known electronic state of CHO is $^2A''$, provisionally regarded as the ground state.[21] This $^2A''$ state cannot be correlated with the $^1A_1$ ground state of formaldehyde (Table 2), or with a stable excited state of formaldehyde because none is available; it must correlate with a dissociative state. Conversely, the unstable $^eA'$ state of formaldehyde must correlate with the $^2A''$ state of formyl unless there exists another, very low-lying, state of formyl at present unknown. The adiabatic dissociation

$$CH_2O^* \, (^eA') \longrightarrow H\,(^2S_g) + CHO\,(^2A'') \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is permitted (Table 2) because the reactant and the product have no common element of symmetry. In terms of one-electron wave functions, the lowest $^eA'$ state of formaldehyde results from a π–π' promotion (expected to lead to a strongly pyramidal state [22])

$$\begin{aligned} &KK\,(\sigma_1, a_1)^2(\sigma_2, a_1)^2(\sigma_3, a_1)^2(\sigma_4, b_2)^2(\pi, b_1)^2(n, b_2)^2 : \, ^1A_1 \longrightarrow \\ &\qquad KK\,(\sigma_1, a')^2(\sigma_2, a')^2(\sigma_3, a')^2(\sigma_4, a'')^2(n_1, a')(n_2, a'')^2(n_3, a') : \, ^{1,3}\boldsymbol{A'} \quad . \quad (2) \end{aligned}$$

where n_1, n_2 . . . signify mainly non-bonding orbitals.

Configuration interaction blurs the outline of the representation in (2), but we conclude that the upper state is unstable and that it " crosses " the surfaces of the $^eA''$ state (n–π')

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[20] Schuler, *Spectrochim. Acta,* 1950, **4**, 85.

[21] Herzberg and Ramsay, *Proc. Roy. Soc.*, 1955, *A*, **233**, 34.

[22] Walsh, *J.*, 1953, 2288, 2306.

in the region of the electronic origin.* A consequence of this explanation is that the banded spectrum of formaldehyde should be superimposed on a weak continuum. The dissociation of the ${}^{e}A'$ state according to (1) may explain why the analogue of an $N \longrightarrow V$ transition of formaldehyde has not been satisfactorily identified.

Beyond 2850 Å formaldehyde shows a second, much stronger predissociation,[16, 17] the onset being somewhat above the energy of the first excited, ${}^2\Sigma^+$, state [21] of CHO. The decomposition

$$H_2CO\ ({}^1A_1) \ldots\ldots H\ ({}^2S_g) + HCO\ ({}^2\Sigma^+) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

being permitted, it is natural to correlate the ${}^2\Sigma^+$ state with a dissociation limit of the A_1 ground state of formaldehyde. The second predissociation of the A'' state therefore involves an ${}^{e}A'' \longrightarrow {}^{e}A_1$ radiationless transition to levels of the ground state of formaldehyde above the dissociation limit. The interpretation of both predissociations is summarised in Fig. 2.

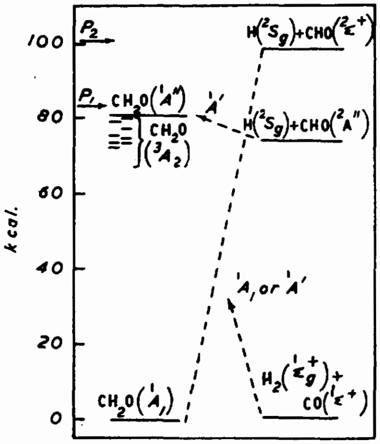


FIG. 2. *Arrows on the left mark the two predissociations in the ^{e}A'' excited state. The short leading lines mark known vibrational levels of a low-lying state, ^{3}A$_2$ or ^{3}A'' (Cohen and Reid,* J. Chem. Phys., 1956, **24**, 85), *of* [^{1}H$_2$]-[19a] *and* [^{2}H$_2$]-*formaldehyde: the position of the zero-point level of this state is uncertain.*

FIG. 3. *The energy scale (ordinate) is relative to the ground state of* CH_2O.

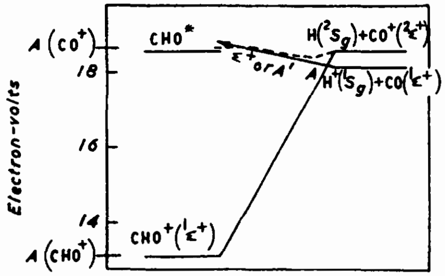
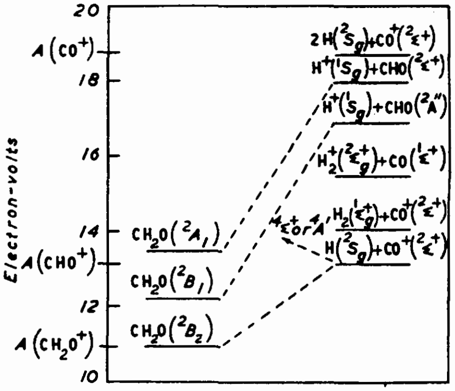


FIG. 4. *Cf. legend to Fig. 3.*



(3) *States of* CHO$^+$.—The ground state of CHO$^+$ is lower in energy than that of the dissociation products (H$^+$ + CO and H + CO$^+$)· by at least 5 ev, in agreement with expectation for the stable electron configuration,

$$KK\sigma_1{}^2\sigma_3{}^2\sigma_3{}^2\pi_1{}^4 : {}^1\Sigma^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In Fig. 3 the dissociation of the ground state is correlated adiabatically with the separated states H (${}^2S_g$) + CO$^+$ (${}^2\Sigma^+$) on the ground that the electron configuration,

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* The mixing potential must have *a''* symmetry. It may be encompassed by a rotation about the axis of least inertia, for it is known from high-resolution measurements that the 1$^-$ level of [^{1}H$_2$]formaldehyde has an abnormal dependence of the rotational energy levels on *K*.[18] But the rotational perturbation may have a different explanation (Part I and ref. [19a]).

$KK\sigma_1^2\sigma_2^2\pi_1^4\sigma_3 : {}^2\Sigma^+$ of CO^+ is precisely that expected to form a strong bond with a hydrogen atom.[23] This correlation is permitted for the dissociation of a linear triatomic molecule through a linear transition state (Table 3). The excited states of CHO^+ will involve the promotion of a π_1 electron (eqn. 3) to an antibonding π_2^1 or σ_4^1 orbital, probably accompanied by reorganisation to a non-linear configuration.[22] According to the electron-impact data the first stable excited state is reached by a vertical excitation of 5·3—5·6 v.

On the assumptions underlying Fig. 3 the separated states $H^+ ({}^1S_g) + CO ({}^1\Sigma^+)$ have to be correlated with an unstable ${}^1\Sigma^+$ or ${}^1A'$ excited state of CHO^+: interaction at the crossing-point A (Fig. 3) is not expected to be unduly great because the electron configurations differ considerably. The production of CO^+ ions, without excess of kinetic energy,[1] may be explained by direct predissociation from the stable excited state, or by induced predissociation through the unstable excited state (*i.e.*, the path indicated by the broken line in Fig. 3). In electron-impact studies, production of ions *without excess of kinetic energy* is a powerful argument in support of a radiationless transition as a step in the mechanism of decomposition.

(4) *States of* CH_2O^+.—The ground and first excited states of CH_2O^+ are stable to possible forms of dissociation, for the states of the separated products, $H + HCO^+$, $H^+ + HCO$, $H_2 + CO^+$, and $H_2^+ + CO$, all lie at considerably greater energy. From the single-electron configurations [9] it would be predicted that the low-lying states of H_2CO^+ are doublet states with the nuclear configuration C_{2v}. The ground state:

$$KK(\sigma_1, a_1)^2(\sigma_2, a_1)^2(\sigma_3, a_1)^2(\sigma_4, b_2)^2(\pi, b_1)^2(n, b_2) : {}^2B_2 \quad . \quad . \quad . \quad . \quad (4)$$

is expected to correlate with the lowest state of the products, $H ({}^2S_g) + HCO^+ ({}^1\Sigma^+)$ (Fig. 4) which, according to the rules in Table 2, may be formed adiabatically from a ${}^2B_2$ or ${}^2A_1$ state of CH_2O^+. On this basis the dissociation energy of the ${}^2B_2$ state (4) is 2·23 ev (Table 1), the low value being explained by the fact that the approach of a hydrogen atom to the ${}^1\Sigma^+$ state of CHO^+ throws a bonding pair of electrons out of the CO bond region.

The second excited state of CH_2O^+ is higher in energy than the dissociation limit of the ground state and to explain the production of HCO^+ ions without excess kinetic energy we must assume a radiationless transition from the first excited state to levels of the ground state above its dissociation limit. If the single-configuration molecular-orbital theory is qualitatively dependable, the first excited state of H_2CO^+ is reached by a $\pi \longrightarrow n$ promotion (eqn. 4) yielding:

$$. \; . \; . \; . \; . \; . \; . \; (\sigma_4, b_2)^2(\pi, b_1)(n, b_2)^2 : {}^2B_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

A radiationless transition from the state (4) to (5) is forbidden as a transition between electronic states. It may occur by coupling with rotation about the figure axis (this would lead to a very feeble predissociation) or as a transition between vibronic states in which non-totally symmetric vibrations of different species are excited in the two electronic states. This type of induced predissociation has not been observed in polyatomic spectra. It is forbidden by the Franck–Condon principle but may attain appreciable probability in the region of a dissociation limit where the potentials are far from harmonic.

APPENDIX

Standard enthalpies of formation, ΔH_f°, *in the gaseous state at* 1 *atm. and* 25° (kcal. mole^{-1}): Hydrogen atoms,[24a] 52·1; carbon monoxide,[24a] −26·42; formyl radical,[1] −4·7; formaldehyde,[24a] −27·7.

Ionisation potentials (electron-volts): hydrogen atoms,[24b] 13·595; carbon monoxide, 14·01; formyl radical,[1] 9·87; formaldehyde,[1] 10·87; hydrogen,[25] 15·43.

Excitation energies (electron-volts): CHO (${}^2\Sigma^+$),[21] 1·05; CH_2O (${}^1A''$), 3·50 (Part I); CO and CO^+, ref.[18], Table 39.

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[*Received, December* 14*th*, 1956.]

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[23] Linnett, *J.*, 1956, 275.

[24] Nat. Bur. Stand., (*a*) Circ. 500, 1949; (*b*) Circ. 467, 1948.

[25] Beutler and Junger, *Z. Physik*, 1936, **100**, 80.