362. *Primary Photochemical Processes. Part III. The Absorption Spectrum and Photochemical Decomposition of Keten.*

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The study of the absorption of light by polyatomic molecules shows that the process is often localised in the first instance in certain characteristic groups, called chromophores: radicals such as the azo-group or the carbonyl group each confer their characteristic absorption spectra upon the molecules of which they form part. In the simplest cases, the effects are confined to the chromophoric group, and the results are analogous to those observed for diatomic molecules; more often, however, the energy may be transmitted with varied results to other parts of the molecule.

Much has been learned of the mechanism and effects of light absorption in diatomic molecules; it is the purpose of the studies in this series to extend the field of observation to polyatomic molecules, and to examine as far as possible from the spectroscopic standpoint the laws governing the photochemical phenomena observed. Processes such as the rupture of a molecule into atoms or radicals form the essentially photochemical part of the majority of photochemical reactions. In some instances the secondary dark reactions which may overtake the primary products obscure the issue by the complexity of the kinetic effects to which they may give rise, as in cases of photo-chlorination; in others they are simpler and less extensive, so that the characterisation of the products of a photochemical decomposition can often be used as a reliable guide in the elucidation of the nature of the primary photochemical change.

A complete study of the primary photochemical effect will therefore endeavour to determine the conditions under which energy transfer occurs from one part of a polyatomic molecule to another, the nature of the chemical processes or fluorescence phenomena induced, and the energy relationships involved. The problems must be attacked from as many angles as possible, but particularly from the spectroscopic and chemical, including the measurement of quantum yields. The data, if sufficiently precise and complete, will form an essential part of the raw material for the quantitative study of molecule building by the methods of quantum mechanics and wave mechanics.

Keten, which forms the subject of the present communication, has the advantage of being obtainable in the gaseous monomeric form, and its structure, comparable with that of carbon dioxide, is sufficiently simple and well established from the chemical standpoint to provide a basis for the interpretation of the photochemical phenomena observed. The experimental work which follows is divided into two sections: the analysis of the products of the photochemical reaction and the measurement of the absorption spectrum. There result the following very simple observations. (1) The light absorption responsible for the photochemical change observed occurs in a region of the spectrum which is characteristic of the $>C=O$ (and not the $>C=C<$) group. (2) The products of the photochemical change consist solely of ethylene and carbon monoxide in the ratio of 1 : 2 by volume. These results lead to the conclusion that, although the initial light absorption occurs in the keto-group, yet the energy is passed to the ethylenic link, where rupture of the molecule occurs: $H_2C{:}CO \longrightarrow H_2C + CO$. The liberated methylene radicals then rapidly attack new keten molecules: $H_2C + CH_2{:}CO \longrightarrow C_2H_4 + CO$, so the integrated result of the absorption of one light quantum is $2H_2C{:}CO + h\nu = C_2H_4 + 2CO$. The character of the absorption spectrum, which consists of diffuse bands, is in accord with this interpretation, as will appear from the subsequent discussion.

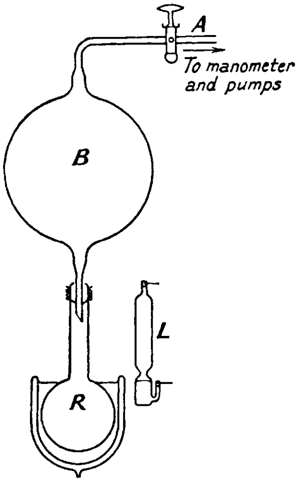
Experimental.

Preparation of Keten.—Keten was prepared by the thermal decomposition of acetone (Hard and Tallyn, *J. Amer. Chem. Soc.*, 1925, **47**, 1427). Commercial acetone, once redistilled, was vaporised in a bath of boiling water, and passed at a rate of about 20 c.c. per minute through a Pyrex tube about 2 ft. long, which was filled with broken pumice and heated in an electric furnace to 700°. The issuing gas passed in order through a double-surface water-cooled condenser, a glass trap, a spiral cooled in solid carbon dioxide–ether, and was then condensed in a trap cooled in liquid air. Free acetone and water and other condensable products were removed by the cooled spiral, about four-fifths of the acetone being recovered unchanged; the crude product contained much ethylene and some higher olefins.

The trap containing the keten was sealed off, and attached directly to the decomposition apparatus; it was then immersed in a pentane bath at — 145° to — 150° and evacuated completely by means of a Toepler pump in order to remove the ethylene. The residual keten was distilled at — 78° (solid carbon dioxide and ether) into a trap cooled in liquid air, the middle fraction only being retained. Before the photochemical decomposition of the gas was investigated, samples were removed by means of the Toepler pump, and the keten estimated by absorption by caustic potash, and also by bromine water; it was found to be 98% pure, the residue consisting of hydrocarbons, mainly propylene.

The Photodecomposition of Keten.—The apparatus used in studying the decomposition is illustrated in Fig. 1. A quartz flask *R* of 100 c.c. capacity, with a neck about 15 cm. long and 2 cm. in diameter, was attached by a ground joint to a large glass globe *B* of 1 l. capacity. The globe was connected to a manometer, a water pump, a Toepler pump, and to the liquid-air trap containing the purified keten. The irradiation of the keten vapour was carried out by a vertical pattern mercury lamp *L* placed parallel to the neck of the quartz flask and about 10 cm. distant from it. The lamp was run off a 220-volt direct-current circuit at a terminal voltage of 150, and a current of 3·5 amps.

FIG. 1.



The apparatus having been completely evacuated by means of the Toepler pump, 2—3 c.c. of liquid keten were distilled into the quartz flask by the cooling of the latter in a bath of liquid air. The liquid air round the bulb of the flask was then replaced by a paste of solid carbon dioxide and ether; by this means a vapour pressure of keten of about 110 mm. was obtained. The pressure was noted, and the tap *A* turned off. The irradiation was then commenced, the bulb of the flask being always kept in the freezing mixture; illumination was continued for 6 hours in one instance and 3 hours in another. The gases formed in the decomposition collected mainly in the large globe. They were separated into three fractions by pumping off (1) through a trap cooled in liquid air, (2) through a trap cooled in a pentane bath to — 150°, and (3) at room temperature. The fractions were collected in Lunge nitrometers and analysed completely (Treadwell and Hall, " Quantitative Analysis," Wiley and Sons, 1919). The first consisted of pure carbon monoxide; the second was divided into two portions, one of which was practically completely absorbed by bromine water, while the other was exploded with excess of oxygen and identified as pure ethylene. The third fraction had the same composition as the sample of keten put into the apparatus, and consisted therefore of the unchanged reactant. One experiment was carried out with a filter of vita glass interposed between the lamp and the decomposition flask, thus admitting only light of longer wave-length than 3000 Å.U.; decomposition still occurred, however, with this range of light. In each case carbon monoxide and ethylene were formed in the decomposition in the proportion of 2 : 1 by volume. Results are shown in Table I.

TABLE I.

Time of illumination, hours.	c.c. at N.T.P.			Composition, %.	
	Vol. of decompn. products.	CO.	C_2H_4.	CO.	C_2H_4.
6	20·25	12·4	6·0	61·3	29·6 *
3	12·24	8·2	4·04	67	33
14 (vita-glass filter)	3·6	2·45	1·15	68	32

* In consequence of a slight leak of air into apparatus when the second fraction was being pumped out, the percentages of CO and C_2H_4 in this experiment do not add up to 100.

Partial polymerisation of the keten occurred, mainly on the walls of the large globe; this was a purely dark reaction which occurred equally well in the unilluminated part of the apparatus. A brown resinous mass was formed upon the wall of the quartz flask nearest the lamp as a result of the action of the light upon the solid polymerised keten. This was insoluble in ether or alcohol, but was removed in suspension in water by rubbing with a glass rod. It was not examined further.

We may therefore represent the photochemical decomposition of the monomeric form of keten by the equation $2CH_2{:}CO = C_2H_4 + 2CO$.

The Absorption Spectrum of Keten.—Photographs of the absorption spectrum of keten were obtained, using the first order of a concave Rowlands grating of 3 m. focal length. The grating was erected in a Rowlands mounting, and gave a dispersion of 5·3 Å.U. per mm. A hydrogen lamp, consuming 3 kw. and giving a continuous spectrum from 4000 to 2000 Å.U., was employed as light source. The absorption tube was constructed in quartz with plane end-pieces fused on, and was 1 m. long; it could be completely evacuated by means of a mercury diffusion pump, and filled with keten vapour to any desired pressure by putting it into communication with a side-tube reservoir cooled in a freezing mixture of suitable temperature. Keten of 98% purity, prepared as described above, was distilled into a reservoir kept cool in liquid air; from the reservoir a convenient quantity was distilled to the side tube, from which the absorption tube was filled; convenient pressures were found to be (1) atmospheric (side tube at − 55°), (2) *ca.* 110 mm. (side tube at − 78°), using solid carbon dioxide and ether in each case.

The absorption spectrum was found to consist of two parts: first, a series of completely diffuse bands, each approximately 12 Å.U. wide, extending from 3706 Å.U. to 2601 Å.U.; secondly, a weakly marked region of continuous absorption which commenced at *ca.* 2200 Å.U. and extended to the limit of emission of the hydrogen lamp (2000 Å.U.). The latter region was separated from the former by a region of transparency (2600—2200 Å.U.); it was structureless under all conditions of observation, and its limit difficult to characterise.

With keten at atmospheric pressure, the absorption in the first region was continuous between 3580 and 2960 Å.U., but at 110 mm. the whole of this became resolved into diffuse bands. The first and last bands were exceedingly faint, but at no point was any fine structure observable; the approximate positions of the bands as measured by a travelling microscope (mercury spectrum as standard) are given in Table II.

TABLE II.

Keten : Diffuse Absorption Bands.

Wave-length, Å.U. (Lardy.)	Wave-length, Å.U. (Present authors.)	Wave-numbers, in vacuo. (Present authors.)	$\delta\nu$.
3850			
3784			
3720			
3658	3700	27,019	453
3610	3639	27,472	500
3565	3574	27,972	453
3505	3517	28,425	352
3465	* { 3474	28,777	
	3469	28,818	379
3413	3424	29,197	310
3382	3388	29,507	879
3283	3290	30,386	431
3238	3244	30,817	336
3204	3209	31,153	294
3161	3179	31,447	381
† 3134	3141	31,828	369
	3105	32,197	314
	3075	32,511	363
	3041	32,874	317
	3012	33,191	481
	2969	33,672	401
	2934	34,073	376
	2902	34,449	360
	2872	34,809	305
	2847	35,114	425
	2813	35,539	318
	2788	35,857	390
	2758	36,247	305
	2735	36,552	351
	2709	36,903	358
	2683	37,261	393
	2655	37,654	343
	2631	37,997	350
	2607	38,347	

Lardy's wave-lengths refer to the short wave-length side of the bands. The authors' figures refer to the centre of the bands.

* This appears to be a doubtful double band.

† Lardy records no bands below this.

The absorption of keten has also been observed by Lardy (*J. Chim. physique*, 1924, **21**, 353), who characterises the two regions of absorption, described above, the second beginning at about 2300 Å.U. The former is shown to be characteristic of the carbonyl group, and the latter of the olefinic group. His general observations are confirmed by us, though our measurements of the diffuse bands extend much further than those formerly recorded.

DISCUSSION.

The interpretation of the data of the present paper raises several points of interest. There can be little doubt that the banded absorption spectrum observed between 3700 and

2600 Å.U. is primarily to be associated with the carbonyl group, though its position has been somewhat modified by the specific structure of the keten molecule. Thus, while the absorption of ketones as a group is located in general approximately between $\lambda\lambda$ 3400 and 2500 Å.U., with a maximum at *ca.* λ 2800, that of keten is displaced about 200 Å.U. towards the long-wave end of the spectrum. This change is small, in view of the modification of structure associated with the immediate juxtaposition of the olefinic double bond to the carbonyl group. The region of absorption associated with the olefinic double bond, on the other hand, as represented by ethylene,[*] is more remotely situated at *ca.* $\lambda\lambda$ 2100. According to Lardy (*loc. cit.*), this appears in the absorption spectrum of solutions of keten, at wave-lengths less than 2300 Å.U. and, as recorded above, we were able to confirm the existence of an absorption by the vapour of keten for wave-lengths shorter than 2200.

The diffuse character of the spectrum in the near ultra-violet indicates that we are here dealing with a type of predissociation. There is, however, no transition from a region of discrete structure, as in other cases of pre-dissociation. The bands are diffuse throughout, and appear more or less symmetrical, showing no marked shading in any direction; they constitute a succession of small continuous absorption spectra, and their character is probably associated with the fact that, whereas the first act of absorption is effected by the carbonyl group, there exists a very high probability of a radiationless transfer of the absorbed energy to the neighbouring olefinic bond. This occurs, with consequent rupture of the molecule at that point. The gross vibrational structure of the carbonyl group is thus impressed on the absorption band, while the absence of any discrete structure indicates that the probability is such that the transfer of energy away from the carbonyl group and the rupture of the molecule occur inside the natural period of one rotation.

This conception of energy transfer from one group in the molecule to another is strongly supported by the character of the induced photochemical decomposition; the analytical data recorded above show that, in the vapour phase, the monomeric molecule gives quantitatively two volumes of carbon monoxide and one of ethylene, and that the whole of the absorption region is effective. No trace of oxygen is detected, as would be the case if the carbonyl group itself had any tendency to decompose. This process is only explained in a satisfactory way as a rupture of the molecule at the olefinic bond, to give molecules of CH_2 and CO. The methylene molecules, being unstable, attack further molecules of keten, to give ethylene. The complete process may thus be written: (1) $H_2C{:}CO + h\nu = CH_2 + CO$; (2) $H_2C{:}CO + CH_2 = C_2H_4 + CO$, only the former being light sensitive.

The characterisation of the photochemical change in this manner raises certain considerations of the availability of energy on photodecomposition which are of considerable theoretical importance. The diffuseness of the spectrum indicates that molecular decomposition is effected throughout the whole absorption region of keten; the minimum quantum effecting decomposition thus corresponds to $\lambda = 3850$ Å.U., representing 74 kg.-cal. per g.-mol. The energy of rupture of the double bond is, however, of the order 167 kg.-cal.,[†] so that the energy of the light is less than half that required to disrupt the

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[*] Ethylene vapour absorbs from 2100 Å.U. to shorter wave-lengths (Stark, Steubing, Enklaar, and Lipp, *Jahrb. Radioakt.*, 1913, **10**, 139; Ludlam and Mooney, *Trans. Faraday Soc.*, Aug. 1929).

[†] The energy values of the chemical bonds of carbon given in the tables of Sidgwick and Bowen (*Ann. Reports*, 1931, **28**, 401) are based on dissociation of the molecule to the ^3P (normal) state of gaseous carbon, 150 kg.-cals. being taken as the heat of sublimation of graphite to the vapour (^3P). While there is no reason to revise this value of the heat of sublimation of carbon, which is now confirmed from several independent sources, it is important in calculating the energy value of bonds, for photochemical processes, to take account of the fact that molecular dissociation must be imagined to occur to the quadrivalent (^5S) state of carbon. The difference between the ^5S and the ^3P state is 1·6 volts, *i.e.*, 37 kg.-cals. (Heitler and Herzberg, *Z. Physik*, 1929, **53**, 52). Thus, for calculations involving the rupture of bonds in molecules, Sidgwick and Bowen's values for all C–X bonds must be increased by 9·25 kg.-cals., each C–C bond by 18·5 kg.-cals., and each $C{:}C$ by 37 kg.-cals. An example will make this clear: the data of Sidgwick and Bowen give for the C–H link 93·6 kg.-cals. This means that if the four hydrogen atoms are removed from methane, and the resulting quadrivalent (*i.e.*, ^5S) carbon atom allowed to change to the bivalent (*i.e.*, ^3P) condition, the energy absorbed will be 93·6 × 4 = 374·4 kg.-cals. The heat of rupture of a single hydrogen atom *per se*, to leave a methyl group, must

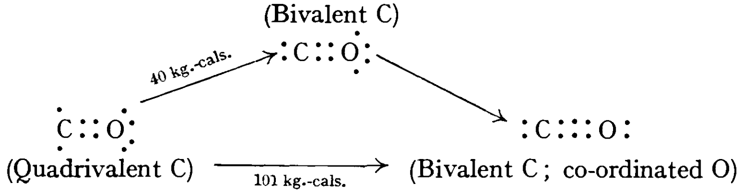
molecule into free radicals. Even if we take the shortest wave-length of the absorption region, *viz.*, 2600 Å.U., the magnitude of the corresponding quantum—110 kg.-cal. per g.-mol.—is still too small.

We are thus brought to the conclusion that the radicals are not liberated with free valencies, but only after some reorganisation, in which energy is liberated. For the $>CO$ radical, this change may be represented as $>CO \longrightarrow C \stackrel{\leftarrow}{=} O$, *i.e.*, as a change from quadrivalent to bivalent carbon. For the $>CH_2$ radical, a similar change will probably occur: $>CH_2 \longrightarrow CH_2$. The magnitude of the amounts of energy liberated in these processes can only be estimated approximately; they will be roughly of the same order as the energy difference between the ^5S and the ^3P state of the carbon atom, and represent in terms of the Heitler–London theory a change from a state in which there are four valency electrons (quadrivalent carbon) to one in which there are only two, the other two being paired with opposite spins (bivalent carbon). The energy difference between these two atomic states of carbon has been given by Heitler and Herzberg (*loc. cit.*) as 1·6 volts, *i.e.*, 37 kg.-cals. per g.-mol.

Thermochemical calculation, however, gives a value for the energy of reorganisation of $>CO$ considerably in excess of this value. Thus from the thermochemical equations

$$\begin{array}{rlrl} & H_2CO \longrightarrow H_2 + CO & +\,2 & \text{kg.-cals.} \\ & H_2CO \longrightarrow H + H + {>CO} & -\,206 & \text{kg.-cals.} \\ & H_2 \longrightarrow H + H & -\,103 & \text{kg.-cals.} \\ \text{we obtain} & {>CO} \longrightarrow C \stackrel{\leftarrow}{=} O & +\,101 & \text{kg.-cals.} \end{array}$$

This greater value may be accounted for by the fact that the former considerations giving about 40 kg.-cals. take account only of the change from quadrivalent to bivalent carbon, while in the forming of the stable carbon monoxide molecule there must be a further liberation of energy due to the formation of the co-ordinate link with oxygen. These changes may be formally represented as:



We shall thus take the energy of reorganisation of the $>CO$ radical as 101 kg.-cals., and of the CH_2 radical as about 40 kg.-cals., the total energy set free thus being approximately $101 + 37 = 138$ kg.-cals.

If, now, the whole primary photochemical change be visualised as a direct passage from the keten molecule to the free molecules CH_2 and $C \stackrel{\leftarrow}{=} O$ in one act, the total energy absorbed by the change will be given as the difference between the value of the double bond and the energy of reorganisation, *i.e.*, $(167—138) = 29$ kg.-cals., a quantity which is not in excess of the minimum photochemical quantum (74 kg.-cals.) available. In terms of Heitler's theory of "spin-valenz," we might formulate this change as a simple change in the pairing of the electron spins of the olefinic group, the molecules CH_2 and CO being liberated in singlet states. Since the magnitude of the absorbed quantum is greater than the minimum required, the free molecules will move apart with excess energy of vibration or translation.

The essential ideas underlying the above analysis of the primary change in keten thus involve: (1) absorption of the light quantum by the $>CO$ group; (2) transfer through some process of coupling to the olefinic group; (3) decomposition of the double bond through a change in the atomic state of carbon from one of quadri- to one of bi-valency, a process which can be visualised as occurring simply, and in one act. The energy of this

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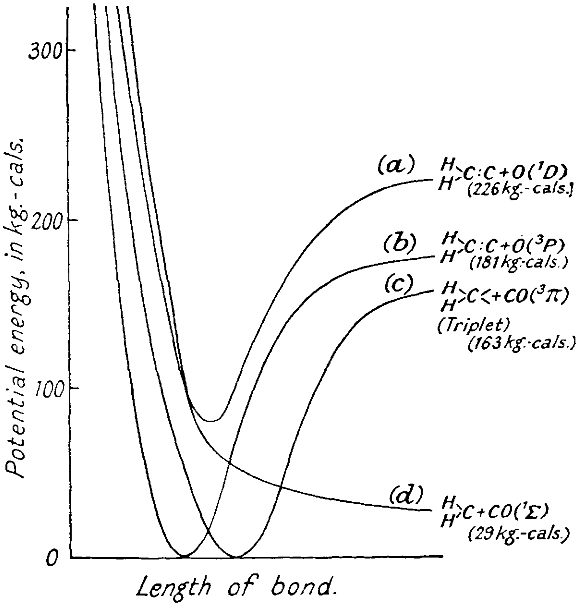
therefore be adjusted for the energy emitted when carbon passes from the ^5S to the ^3P state, *i.e.*, 37 kg.-cals. The value of the bond is thus $(374{\cdot}4 + 37)/4 = 102{\cdot}8$ kg.-cals. The values given by Sidgwick and Bowen, modified as described above, have been used in the present paper.

change, although it cannot at present be calculated accurately, can be estimated as being in accord with the magnitude of the minimum effective photochemical quantum.

The whole of the primary photochemical process for keten may be represented by the potential energy diagrams in Fig. 2, in which the energy values are given roughly to scale. Curve (*b*) represents the potential energy of the $>CO$ group in keten in the ground state, plotted as a function of the distance between the carbon and oxygen atoms. The molecule will dissociate ultimately into a normal oxygen atom and a free radical. This process would represent the thermal dissociation of the carbonyl group in keten. Curve (*a*) is the potential curve for the first excited state of the carbonyl group, culminating in the photochemical dissociation into a free radical and an excited oxygen atom. Transitions from the curve (*b*) to the curve (*a*), however, never result in a stabilised upper level, and the above photochemical dissociation does not occur, since for all the vibrational levels of curve (*a*) there exists the probability of an energy switch to curve (*d*) representing the potential energy curve of CH_2 and CO molecules involving bivalent carbon. In order that this may be the case, curve (*d*) must run very close to and nearly parallel to the left-hand side of curve (*a*). This curve has no minimum, and the molecules thus mutually repel from each other's spheres of action. Curve (*c*) is the potential curve of the olefinic group in the ground state. It indicates that the energy of dissociation to free radicals is much greater than that of dissociation to molecules (*d*). The diagram further suggests that the *thermal dissociation* of keten should occur as a primary process in one act involving predissociation from curve (*c*) to curve (*d*).

FIG. 2.



It is probable that with the development of the quantum-mechanical conception of polyatomic molecules, greater definiteness will be given to some of the ideas tentatively expressed above. In particular, it would be of interest to enquire into the nature and mechanism of the energy switch which apparently occurs from the $>CO$ to the $>C=C<$ group within the keten molecule. This cannot be done until we have a clearer conception of the electronic structure of the molecule in terms of the wave-mechanical conceptions of Lennard-Jones, Mulliken, and Hund, and in particular, in the present instance, how the electrons of the carbonyl and olefinic groups mutually affect each other. It does not seem too much to hope that in the near future some insight into these questions will be gained on the theoretical side.

SUMMARY.

(1) The photochemical decomposition of monomeric keten vapour occurs in light of the mercury lamp. The products are two volumes of carbon monoxide and one of ethylene.

(2) The absorption spectrum of keten vapour consists of a series of completely diffuse bands, occurring fairly regularly between 3700 and 2600 Å.U., the region of maximum absorption occurring round 3100 Å.U.

(3) The primary change is simply interpreted as a splitting of the molecule at the olefinic bond, according to the equation $CH_2{:}CO + h\nu = CH_2 + CO$, the liberated CH_2 molecules reacting further with undecomposed keten, to give ethylene and carbon monoxide, $CH_2{:}CO + CH_2 = C_2H_4 + CO$.

(4) The character of the spectrum suggests that light is first absorbed by the carbonyl group, and that an energy switch occurs to the olefinic group, with the consequent rupture of the molecule.

(5) The energy relationships of the primary change when analysed show that it cannot be represented purely as a rupture of the olefinic bond; they are, however, consistent with a decomposition into CH_2 and CO molecules, each containing carbon in the bivalent form. It is suggested that the decomposition can be simply visualised as taking place in one act by a rearrangement of the electrons constituting the olefinic bond.

(6) The photochemical change is further discussed in terms of potential-energy diagrams.

The authors have had the advantage of discussing the contents of this paper both with Professor J. E. Lennard-Jones, F.R.S., and with Dr. N. V. Sidgwick, F.R.S., to whom they would express their thanks for useful criticism. They are indebted to the Royal Society and the Chemical Society for grants, to the Department of Scientific and Industrial Research for an assistantship, and to the Governing Body of Girton College, Cambridge, for the award of a Yarrow Studentship to one of them (O. S.).

[*Note added, November* 11*th*, 1933.]

A recent paper by Kronig, Schaafsma, and Peerlkamp (*Z. physikal. Chem.*, 1933, *B*, **22**, 323) on the absorption spectrum of chromyl chloride suggests an alternative explanation of the type of diffuse spectrum of keten described above, and it will be convenient here briefly to consider the matter. According to these authors the absorption spectrum of chromyl chloride consists of five parallel sets of equally spaced diffuse bands extending from λ 6000 Å.U. to the violet.

The spectrum has apparently much in common with the spectrum of keten; for both show diffuseness throughout their whole range and there is no marked shading of the bands. Arguing that with predissociation we should expect a threshold, Kronig, Schaafsma, and Peerlkamp assume that we are here dealing with a new type of spectrum, and attribute these diffuse bands to a transition between a stable ground level, and an upper unstable level in which there is preserved a certain quantisation.

In the particular case of keten, however, the explanation given in our paper is consistent with the absence of a predissociation threshold, and is to be preferred by reason of the following considerations. A transition such as that imagined by Kronig would have to be confined to the $>C=C<$ group, since primary rupture of the molecule, as we have shown, occurs here. On the other hand the absorption observed which is responsible for the photodecomposition is a characteristic of the carbonyl group, and completely distinct from the well-established absorption of the C=C group (*loc. cit.*), also present in the keten absorption spectrum in the far ultra-violet. It is thus clear that a radiationless transfer of energy must occur within the molecule from the C:O link to the C:C link in order that the observed products of decomposition may be obtained. Such a process must involve the intersection of two upper levels, and is identical with our conception of predissociation.

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[*Received, July* 28*th*, 1933.]