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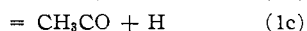
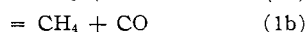
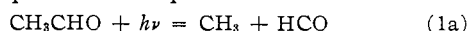
Energy Dissipation from Excited Acetaldehyde Molecules¹

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Energy dissipation in acetaldehyde vapor following absorption at various wave lengths from 2537 to 3340 Å. has been studied. At the longer wave lengths dissociation and intersystem crossover to the ground state from a triplet state account for most of the dissipation. At shorter wave lengths dissociation becomes of increasing importance. This dissociation probably occurs from high vibration levels of the singlet state but the possibility of rapid transition through a triplet state cannot be excluded. As shown previously by other authors, the mode of dissociation changes with wave length.

The photochemistry of acetaldehyde vapor has been very extensively studied.³ Three different primary processes may occur with varying degrees of relative importance dependent on experimental conditions



Hydrogen is a very minor product in the wave length region under investigation and hence (1c) is almost certainly of little importance. Conclusive evidence for (1a) has been found by flash photolysis⁴ and (1b) is proved by the use of scavengers.⁵ Since monochromatic light was not used for flash photolysis and since scavengers affect the magnitudes of primary quantum yields to unknown extents, the relative importances of (1a) and (1b) must still be considered to be unknown. The problem in acetaldehyde is more complicated than it is in the simple ketones because even at temperatures near room temperature a radical initiated chain reaction occurs and yields are difficult to relate to primary quantum yields.

The absorption spectrum of acetaldehyde vapor has also been extensively investigated.⁶ Absorption extends from 3484 Å. to about 2350 Å., with no definite spectroscopic evidence that any part of this region consists of a continuum. Other absorption regions at shorter wave lengths need not concern us here.

Emission from acetaldehyde also has been investigated. It extends from about 3500 to about 4800 Å.^{7,8} A brilliant green emission is associated with the presence of biacetyl,⁹ which is one of the photochemical reaction products.

(1) This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract AF 49(638) 679.

(2) National Institutes of Health Predoctoral Fellow 1960-1962.

(3) For reviews see W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 340, and E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, pp. 284-306. The early work of P. A. Leighton and F. E. Blacet, *J. Am. Chem. Soc.*, **55**, 1766 (1933), has been followed by several papers by Blacet and his collaborators as well as from other laboratories. References will be given in the present article only to those publications germane to the particular aspects of the photochemistry of acetaldehyde being discussed.

(4) G. Herzberg, *Proc. Chem. Soc. (London)*, 116 (1959).

(5) F. E. Blacet and D. J. Heldman, *J. Am. Chem. Soc.*, **64**, 889 (1942); F. E. Blacet and D. E. Loeffler, *ibid.*, **64**, 893 (1942); A. S. Buchanan, *J. Chem. Soc.*, 2317 (1951).

(6) S. A. Schou, *J. chim. phys.*, **26**, 27 (1929); E. Eastwood and C. P. Snow, *Proc. Roy. Soc. (London)*, **A149**, 434 (1935); V. R. Rao and I. A. Rao, *Indian J. Phys.*, **28**, 491 (1954). See also P. A. Leighton and F. E. Blacet, ref. 3.

(7) E. Murad, *J. Phys. Chem.*, **64**, 952 (1960); Ph.D. Thesis, University of Rochester (1959).

(8) P. Longin, *Compt. rend.*, **251**, 2499 (1960).

(9) M. S. Matheson and J. W. Zabor, *J. Chem. Phys.*, **7**, 536 (1939).

While light emission in this instance is a minor means of energy dissipation, the existence of an emission often leads to useful conclusions concerning the fates of various excited states of absorbing molecules. The present work was undertaken to attempt to assess the roles of singlet and triplet states of acetaldehyde in its photochemistry. Toward the long wave length end of the absorption region both singlet and triplet emission occur. The use of nitric oxide as a scavenger permits some conclusions to be drawn but since it quenches triplet emission it may also have an effect on the magnitude of any primary dissociation which may arise from that state. Further work on primary quantum yields is badly needed but this would be of little value unless proper methods for such studies can be developed.

Experimental

Eastman Grade acetaldehyde, Eastman Grade biacetyl, and Eastman Spectro Grade acetone were degassed and distilled bulb-to-bulb in a grease-free high vacuum system. The middle third was retained for use in each case. Analysis by vapor-phase chromatography showed the acetaldehyde and the biacetyl to be about 99.7% pure. No impurities could be detected in the acetone by a similar analysis.

The impurity in acetaldehyde had no effect on acetaldehyde emission. This was determined by observing emission from acetaldehyde specially purified by collection from a vapor-phase fractometer.

Matheson nitric oxide was purified by repeated vacuum distillation from a bulb at -159° to a bulb at -195° . No impurities were detectable by mass spectrometric analysis. Airco Reagent Grade oxygen and Phillips Research Grade methane were used without further purification.

A conventional glass high vacuum apparatus free from stop-cock grease was used for all experiments. The quartz cell was T-shaped, with each of its three windows 22 mm. in diameter. The area of the exciting radiation incident on the cell window was limited by a 14 mm. diameter diaphragm to about 1.56 cm.². This diaphragm reduced reflection of incident radiation from the walls of the cell. The path length of the incident light beam in the cell was 56 mm. The volume of the cell section (including a magnetically operated stirrer and connecting tubing) was about 190 ml. The cell was encased in an electrically heated aluminum block furnace.

An Osram HBO-500W high pressure mercury arc lamp was used for all emission experiments and for all photolysis experiments at wave lengths other than 2537 Å. A Hanovia S-100 mercury arc lamp was used for photolysis experiments at 2537 Å. The desired wave lengths were isolated from these sources by a Bausch and Lomb Grating Monochromator with a linear dispersion of 33 Å., per mm. Light from the monochromator was collimated and after passage through the cell was focused on an RCA 935 phototube by quartz lenses.

With the monochromator slit widths generally used in these experiments, the total radiation in the incident beam in the cell from the Osram lamp (expressed in photons per ml. per second) was about 5×10^{14} at 3340 Å., about 1×10^{14} at 3130 Å., about 5×10^{13} at 2967 Å., and about 1×10^{13} at 2804 Å. The intensity at 2537 Å. from the Hanovia S-100 lamp was about 1×10^{12} quanta per ml. per second. These calculations are based on a light beam volume of 9.74 ml.

Photographs of the emission spectra were taken with a Hilger Quartz Spectrograph Model E-484. This instrument has a linear dispersion of about 100 Å. per mm. at 4200 Å. and a slit width of 0.1 mm. Eastman Spectroscopic Plates Type 103-O and Type 103-F were used to photograph acetaldehyde and biacetyl emission, respectively. Tracings of the image were made with a Sinclair Smith Recording Microphotometer.¹⁰ The positions of the band centers in the emission spectrum were determined from these tracings. Lines from a mercury arc were superimposed on portions of each spectrum to serve as calibration points. All bands (particularly those at wave lengths longer than 3700 Å.) are broad and weak and for this reason the centers of the bands were chosen somewhat arbitrarily.

The addition and mixing of gases followed procedures previously used. Gases were continuously circulated in the cell during each experiment by a magnetic stirrer. Acetone vapor at 125° was used as an actinometer for the photolysis experiment at 3130 and at 2537 Å. The carbon monoxide from the acetone photolysis was determined by methods described previously.¹¹

Absorption (I_a') was determined in arbitrary units as the difference between the light transmitted through an empty cell and the light transmitted through the cell filled with gas. The transmitted light was measured by an RCA 935 phototube connected to a Varian G-10 ten-mv. recorder. The spectral sensitivity of this tube was specially calibrated by the manufacturer. Since the entire transmitted beam was focused to a spot on the cathode of the phototube and since the cathode appeared to have a uniform sensitivity over its surface, I_a' is to a very close approximation proportional to the absolute number of photons absorbed per ml. per second.

For experiments used to determine the absolute emission yields (efficiencies) of acetaldehyde (Table I), the intensity of emission (I_e') was measured in arbitrary units by an RCA 1P28 photomultiplier tube whose spectral sensitivity was specially calibrated by the manufacturer. For all other emission experiments, an RCA 1P21 photomultiplier was used. A Corning 7380 filter placed between the emission window and the photomultiplier tube reduced scattered incident radiation to a negligible level. Emission intensities always were corrected for the dark current. The circuits used for these tubes have been described elsewhere.¹¹ Exposure of acetaldehyde to exciting radiation was limited to about three seconds per measurement in all emission experiments. This procedure was necessary to preclude interference by emission from biacetyl which forms as a product of the photolysis.

The gases non-condensable at -215° from the photolysis of the acetaldehyde-nitric oxide mixtures (H₂, CO, CH₄ and N₂) were collected with a Toepler pump and analyzed on a Consolidated Electrodynamics Corporation Model 21-620 Mass Spectrometer. The condensable fraction was vaporized and refrozen several times during collection of the non-condensables to free gases trapped in the frozen materials. (Acetaldehyde polymerizes to a gelatinous material when condensed at temperatures lower than -123°.¹²) Quantitative determinations of methane were based on calibrations of the m/e 15 peak. Correction for day-to-day variations in the sensitivity of the mass spectrometer was made by observing the m/e 14 peak from a known amount of air introduced after each analysis.

Results

(a) **The Emission Spectrum of Acetaldehyde.**—Identical emission spectra were obtained from excitation of acetaldehyde at 3340 and at 3130 Å. and at acetaldehyde pressures from 100 to 400 mm. at 30°. The emission extends from about 3382 to about 5000 Å. with a broad maximum between 4050 and 4200 Å. Weak and diffuse bands can be observed between 3382 and about 4465 Å. This spectrum extends over a wider spectral region than that reported by Murad.⁷ This probably is due to the fact that the emission intensity falls asymptotically to zero on each side of the maximum, and thus, the apparent limits of the spectrum are dependent on the intensity of the emission.

Band centers in the emission spectrum were measured on three different plates. The average frequencies (in cm.⁻¹) of thirteen bands were as follows: 29570,

28800, 28410, 27750, 27090, 26650, 25990, 25250, 24910, 24180, 23470, 23120, 22400.

Experiments were made to establish that the emission truly originated from acetaldehyde. Emission from an impurity appears unlikely since the emission spectrum of acetaldehyde specially purified by collection from a vapor-phase fractometer was identical with the spectrum of acetaldehyde purified by distillation. Emission from a photochemical decomposition product appears unlikely from the fact that the emission spectra below 5000 Å. from a flow system and from a system in which photochemical products were permitted to accumulate during a 24-hour photolysis were identical. Also, the addition of oxygen, which has a marked effect on product formation, had only a small effect on the emission spectrum.

(b) **The Absolute Emission Yield of Acetaldehyde.**

—The absolute emission yield of acetaldehyde (Q) is the ratio of the quanta emitted to the quanta absorbed. Q was determined from the relationship $Q = CI_e'/bI_a'$. I_e' and I_a' are proportional to the number of quanta emitted and absorbed, respectively, per unit time and are expressed in arbitrary units. The quantity b is that fraction of the total number of quanta absorbed which is absorbed in front of the emission window. C is a constant which converts the emission yield from arbitrary units (I_e'/bI_a') to absolute units.

The fraction b was computed approximately from Beer's law. Beer's law is obeyed within experimental error by acetaldehyde and by biacetyl at the exciting wave lengths used in this study. The calculated values of b are approximately constant until the total absorption reaches about 25% and then they begin to decrease rapidly as the bulk of the absorption tends to shift toward the incident window. From this fact it is seen that omission of the factor b would cause the observed emission yields to be artificially low in pressure regions of high absorption. A discussion of this problem has been published previously.¹³

The constant C , which is dependent only upon the geometry of the apparatus and the sensitivity of the phototubes, was determined by observing emission from biacetyl. If one assumes the emission efficiency of biacetyl vapor excited by radiation at 4358 Å. as reported by Almy and Gillette¹⁴ (0.15 ± 0.03) to be correct, C can be derived from the relationship

$$0.15 = CI_e'/bI_a'$$

where I_e' and I_a' are emission and absorption, respectively, from biacetyl vapor excited at 30° by radiation at 4358 Å.

The use of the constant C requires that I_e' and I_a' from acetaldehyde experiments be converted to the same arbitrary units as I_e' and I_a' of the biacetyl experiments. The conversions were made by considering the relative spectral sensitivities of the phototubes, the transmittance of the 7380 filter placed in front of the emission window, and the spectral distribution of biacetyl¹⁵ and of acetaldehyde emission.¹⁶ Since the sensitivity of the phototubes changes only slowly in the spectral regions considered, the conversion of units is probably accurate to within ten per cent.

The absolute emission efficiencies of acetaldehyde at 200 mm. and at 30° resulting from excitation at 3340, 3130, 2967 and 2804 Å. are compared in Table I. The data are the averages of three determinations at each wave length. Acetaldehyde emission was too weak to

(10) This instrument was kindly made available to us by Professor A. B. F. Duncan of this Department.

(11) J. Hecklen, Ph.D. thesis, University of Rochester, 1958; J. Hecklen and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **81**, 3858 (1958).

(12) H. A. Rigby, C. J. Danby and C. N. Hinshelwood, *J. Chem. Soc.*, 234 (1948); R. G. W. Norrish and J. C. Bevington, *Proc. Roy. Soc. (London)*, **A196**, 363 (1949).

(13) F. C. Henriques, Jr., and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **62**, 1083 (1940).

(14) G. M. Almy and P. R. Gillette, *J. Chem. Phys.*, **11**, 188 (1943).

(15) H. Okabe, Ph.D. thesis, University of Rochester (1956); H. Okabe and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **79**, 801 (1957).

(16) See ref. 8 and Fig. 1.

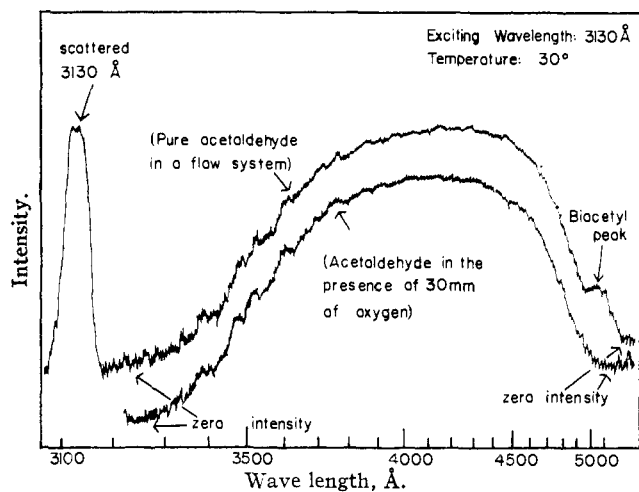


Fig. 1.—Emission spectra of acetaldehyde vapor with and without oxygen present.

observe by a photomultiplier when the exciting radiation was limited to wave lengths between 2537 and 2450 Å. Emission characteristic of acetaldehyde was detected from excitation at these wave lengths, however, by exposing a plate for 161 hours in a Hilger spectrograph with a relatively wide slit (0.5 mm). Wave lengths longer than 2537 Å. could not be detected in a careful check of the exciting radiation. Thus it appears that the acetaldehyde emission is not zero even at these short wave lengths.

TABLE I

EMISSION EFFICIENCIES OF ACETALDEHYDE VAPOR AT 200 MM. PRESSURE AND 30°

Bausch and Lomb monochromator slit widths: 3340 Å. (6 mm.); 3130 Å. (2 mm.); 2967 Å. (1.5 mm.); 2804 Å. (1.5 mm.)

Exciting wave length, Å.	Q^{17}	Standard deviation of Q from the mean
3340	2.79×10^{-3}	0.24×10^{-3}
3130	2.11×10^{-3}	$.38 \times 10^{-3}$
2967	1.49×10^{-3}	$.02 \times 10^{-3}$
2804	1.14×10^{-3}	$.07 \times 10^{-3}$

(c) **Quenching of Acetaldehyde Emission by Nitric Oxide.**—Acetaldehyde emission is extremely sensitive to the presence of nitric oxide. Quenching of emission excited by radiation at either 3340 or 3130 Å. can be observed at nitric oxide pressures as low as 10^{-3} mm. The emission decreases steadily until the nitric oxide pressure has increased to about one mm. Increase of nitric oxide pressure to at least 76 mm. has no further effect on the emission. This behavior is identical with that in the presence of oxygen as reported by Murad.⁷ Furthermore the emission yield of acetaldehyde in the presence of more than one mm. of nitric oxide is identical with that in the presence of more than one mm of oxygen.

Quenching of biacetyl or of acetone emission by oxygen follows this same behavior.¹⁸ The emission strongly quenched by oxygen originates from a triplet state and that portion insensitive to oxygen originates from a singlet state.¹⁹ The oxygen sensitive emission from

(17) It should be remembered that Q is the total number of photons emitted divided by the total number of photons absorbed, *i.e.*, it is a true emission efficiency expressed in photons and not in energy units. For reasons expressed in the text this quantity is not measured directly and hence these absolute values are based on determinations whose true accuracy is hard to assess. More work on accurate methods for determining Q is badly needed.

(18) For a review see W. A. Noyes, Jr., G. B. Porter and J. E. Jolley, *Chem. Revs.*, **66**, 49 (1956).

(19) J. W. Sidman and D. W. McClure, *J. Am. Chem. Soc.*, **77**, 6461, 6471 (1955). Oxygen may exert some quenching effect on singlet states but for those cases for which good data are available this quenching is of a differ-

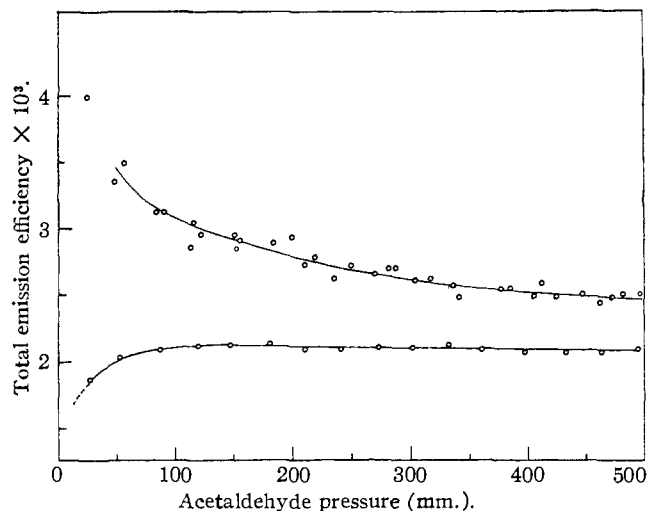


Fig. 2.—Total emission efficiency in acetaldehyde vapor: upper curve, 3340 Å., 30°; lower curve, 3130 Å., 36°.

acetone has characteristics (lifetime and temperature sensitivity) so similar to the triplet emission of biacetyl that it is almost certainly a triplet emission.

By analogy with these compounds, there is little doubt that the emission from acetaldehyde which is quenched either by oxygen or by nitric oxide originates from a triplet state, and that the emission when nitric oxide or oxygen is present at pressures greater than one mm. is singlet emission. Thus, three types of emission efficiencies are reported in this study. Q is the total emission efficiency and is that from pure acetaldehyde. Q_t is the singlet emission efficiency and is that from acetaldehyde in the presence of more than one mm. of nitric oxide. Q_p is the triplet emission efficiency, $Q_p = Q - Q_t$.

The ratio of singlet to triplet emission at 36° and at various pressures of acetaldehyde is given in Table II, for exciting radiation at 3340 and at 3130 Å. The pressure of nitric oxide listed in the table is that used to obtain Q_t . Q_t/Q_p is independent of exciting wave length within experimental error.

A comparison of the emission spectra (Fig. 1) shows that triplet emission of acetaldehyde lies wholly within the spectral region of the singlet emission. Since the sensitivity of the photomultiplier tube is fairly uniform throughout this spectral region, the true ratio of singlet to triplet emission is close to that indicated in Table II.

TABLE II

THE RATIO OF SINGLET TO TRIPLET ACETALDEHYDE EMISSION^a AT EXCITING WAVE LENGTHS OF 3340 AND 3130 Å.

Temp. = 36°			
Acetaldehyde, mm.	Nitric oxide, mm.	Q_t/Q_p 3340 Å.	Q_t/Q_p 3130 Å.
211	5	2.3	2.5
211	12	2.5	2.5
250	6	2.6	2.6
250	13	2.5	2.6
350	5	3.8	3.8
350	14	3.4	3.8
450	5	4.0	3.9

^a Monochromator slit widths were 2 mm. in both cases.

(d) **Emission Efficiencies as a Function of Acetaldehyde Pressure with Exciting Radiation at 3340 and at 3130 Å.**—Figure 2 shows total emission efficiencies at 3340 and at 3130 Å. as functions of acetaldehyde pressure. The temperatures were 30 and 36°, respectively.

ent order of magnitude from that on triplet states. Some caution must be exercised, however, in the interpretation of data.

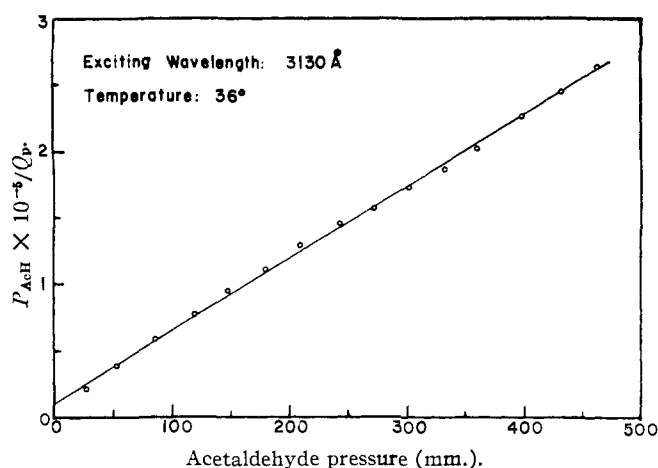


Fig. 3.—A plot of $P_{AcH} \times 10^{-5}$ vs. P_{AcH} acetaldehyde pressure for the singlet emission of acetaldehyde at 3130 Å.

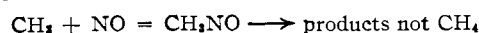
The singlet emission efficiency, Q_i^{3340} , at 3340 Å. is independent of acetaldehyde pressure to within experimental error and is about 0.00214. Figure 3 shows that at 3130 Å. a plot of P_{AcH}/Q_i vs. P_{AcH} , where P_{AcH} is acetaldehyde pressure in millimeters, is approximately linear. The singlet emission efficiency at 3130 Å. was obtained by multiplying the total emission efficiency at 3130 Å. by the ratio Q_i/Q for 3340 Å. at the pressure for which the calculation was made. This ratio was taken from the curve of Fig. 2.

Figure 4 shows the inverse of the triplet emission efficiency from acetaldehyde vapor excited at 3340 Å. This was obtained by subtracting emission in the presence of 6 mm. of nitric oxide pressure from the total emission. Since this is the difference between two relatively large numbers and shows considerable scatter, two sets of points are shown. One set of points used the smooth curve of Fig. 2 for the total emission and the other used actual experimental points. The straight line has been drawn to give the best fit to the former.

(e) **Photolysis of Acetaldehyde-Nitric Oxide Mixtures.**—Photolyses were carried out at 36 and 70° with radiation at 2537, at 3130, and at 3340 Å. Nitric oxide was present at pressures between 200 and 400 mm. The photolysis products non-condensable at -215° were H_2 , CO, CH_4 , and N_2 . Nitrogen was the main component of this mixture and its quantum yield was generally above two.

At 3340 Å. no methane is detectable as a product of the photolysis although carbon monoxide, nitrogen and some hydrogen were observed. Methane was present at 3130 Å., although the amount formed was too small to yield reliable quantitative data. Φ_{CH_4} is about 0.0005 at 3130 Å. and 36°. The quantum yields of methane at 2537 Å. are given in Table III. The quantum yields have been corrected for a dark reaction which apparently occurs when acetaldehyde and nitric oxide are condensed together at -195° before collection of the non-condensable gases.

The emission data show that nitric oxide at pressures less than 75 mm. does not deactivate excited singlet acetaldehyde molecules. Furthermore the rate constants of the reaction



are such²⁰ that about 10 mm. of nitric oxide in 100 to

(20) M. I. Christie, *Proc. Roy. Soc. (London)*, **A249**, 248 (1959); R. W. Durham and E. W. R. Steacie, *J. Chem. Phys.*, **20**, 582 (1952); D. M. Miller and E. W. R. Steacie, *ibid.*, **19**, 73 (1951); W. A. Bryce and K. U. Ingold, *ibid.*, **23**, 1968 (1955); W. C. Steppy and J. G. Calvert, *J. Am. Chem. Soc.*, **81**, 769 (1959); C. N. Hinshelwood, *J. Chem. Soc. (London)*, Special Publ. No. 9, 49 (1957).

TABLE III
THE QUANTUM YIELD OF METHANE FROM MIXTURES OF ACETALDEHYDE AND NITRIC OXIDE AT 2537 Å.

Temp., °C.	Acetaldehyde pressure, mm.	Nitric oxide pressure, mm.	Φ_{CH_4}
36	102	12	0.68
36	100	13	.65
36	204	14	.65
36	205	14	.69
36	200	26	.64
36	200	13	.67
70	224	14	.64
36	400	13	.61
36	400	13	.66
36	400	13	.58
70	449	14	.60
70	448	14	.61
70	448	14	.62

500 mm. of acetaldehyde will suppress the formation of methane from methyl radicals to an undetectable level at temperatures as high as 70°. High yields of nitrogen also have been reported in the photolysis of mixtures of diethyl ketone²¹ and of acetone²² with nitric oxide. It is difficult to suggest any step for meth-

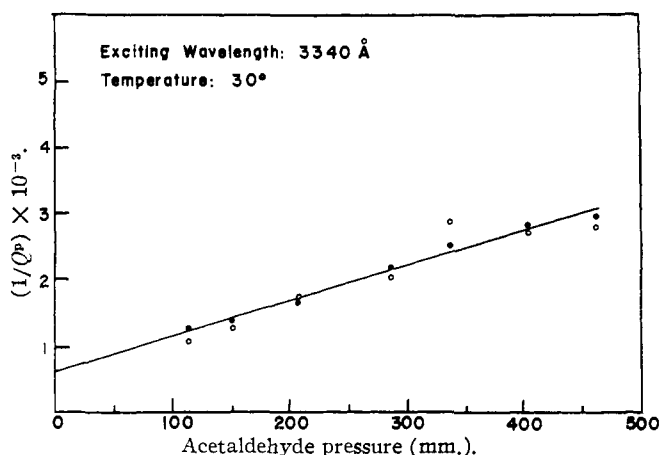
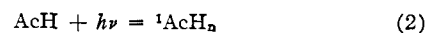


Fig. 4.—A plot of the inverse of the triplet emission efficiency at 3340 Å. vs. acetaldehyde pressure. (Open points use actual values of total emission efficiency to calculate Q_p and the solid points use a smooth curve.)

ane formation in the presence of nitric oxide other than the primary photochemical act. Thus Φ_{CH_4} from acetaldehyde-nitric oxide mixtures almost certainly is a direct measure of ϕ^{1b} from the excited singlet state.

Discussion

Two absorption acts may be visualized



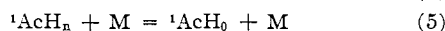
where AcH is a normal acetaldehyde molecule, 1AcH_n is an acetaldehyde molecule in the n 'th vibration level of an excited singlet state, and D represents dissociation products formed so rapidly that the intermediate existence of an excited state need not be postulated. Reaction 3 would imply continuous absorption and reaction 2 banded absorption. This point will be discussed later but the coexistence of these two types of absorption in the spectral region under investigation was proposed by Leighton and Blacet.³ The magnitude of the vibration energy as well as the modes of vibration most prominently excited will depend on wave length for 2.

(21) J. E. Jolley, *J. Am. Chem. Soc.*, **79**, 1537 (1957).

(22) H. W. Anderson and G. K. Rollefson, *ibid.*, **63**, 816 (1941).

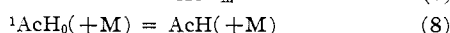
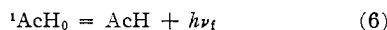
Absorption in aldehydes and ketones in the general region of 2400–3400 Å. is weak so that experimentation is only feasible at pressures of several millimeters. Thus loss of vibration energy by collision will take precedence over all processes except dissociation.

We may write



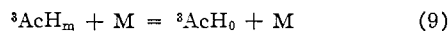
where (4) is a dissociation of such relative speed that it is competitive with (5) and M is a colliding molecule which would be an acetaldehyde molecule in the pure gas. Reasons will be presented shortly for ignoring other reactions of ${}^1\text{AcH}_n$.

The fates of ${}^1\text{AcH}_0$ may be

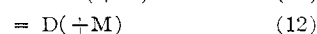
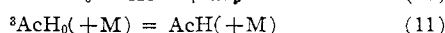
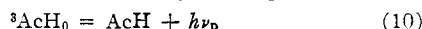


Collisional deactivation of singlet state molecules is a well recognized phenomenon but the internal conversion to the ground state by a process which apparently is first order is more debatable. The present work does not either prove or disprove the occurrence of (8) as a first order reaction. The cross-over to the triplet state by (7) is a well recognized phenomenon. The fact that the ratio of singlet to triplet emission is independent of exciting wave length demands that intersystem crossover and singlet emission originate from the same vibrational levels of the excited singlet state.

Lifetimes of triplet state molecules are generally longer than for singlet state molecules so that one may assume the inevitability of collisional loss of vibration energy



The triplet state molecules may undergo the reactions



The necessity for M in (11) is not certain, but there may be two concurrent cross-overs to the ground state, one of which is and one of which is not dependent on collisions. Reaction 12 apparently requires a small activation energy but collisions may not be rate controlling at the pressures used.

This mechanism leads to the result

$$\phi^I = \frac{k_4 + k_3\phi_3(\text{M})}{k_4 + k_3(\text{M})} \quad (13)$$

where ϕ^I is the total primary dissociation yield from the singlet state, ϕ_3 is the primary yield due to (3) and the subscript for each rate constant corresponds to the reaction number.

If one turns to (6), the emission from the singlet state, one finds

$$\frac{(\text{M})}{Q_f} = \frac{k_4 + k_5(\text{M})}{k_5(1 - \phi_3)} \times \frac{(k_6 + k_7) + k_8(\text{M})}{k_6} \quad (14)$$

where Q_f is the emission efficiency from the singlet state.

The emission from the triplet state (equation 10) is given by the relationship

$$1/Q = \frac{(k_4 + k_5(\text{M}))(k_6 + k_7 + k_8(\text{M}))(k_{10} + k_{11} + k_{12}(\text{M}))}{k_5 k_7 k_1 P(\text{M})(1 - \phi_3)} \quad (15)$$

where Q_p is the emission efficiency from the triplet state.

We may now consider the interpretation of the data at three different wave lengths.

(a) 3340 Å.—At this wave length the amount of vibrational energy in the excited singlet state is small since the 0,0 band for this absorption region is near

3390 Å.²³ Also, since the lifetimes of singlet states are generally short so that dissociation from this state by a unimolecular process would be improbable, there is good reason to believe that there is no singlet dissociation into radicals at 3340 Å. The absence of methane formation in the presence of nitric oxide at 3340 Å. indicates that the excited singlet state does not decompose into molecular products. Hence it is probable that $\phi_3 = k_4 = 0$ at this wave length.

Some unambiguous method of determining the primary yield from the triplet state at 3340 Å. would be desirable. In general triplet state decompositions seem to involve small activation energies.¹⁸ In the case of acetaldehyde, if one assumes variation of Q_p with temperature to be determined by the amount of reaction 12, one could obtain an activation energy, but the uncertainty would be large.⁷

Since at 3340 Å. the vibration level is not far from 0, one may essentially write the absorption act to give ${}^1\text{AcH}_0$. Under these circumstances $Q_f = k_6/(k_6 + k_7)$. At 30° $Q_f = 2.14 \times 10^{-3}$. Hence $k_7/k_6 = 4.7 \times 10^2$. The importance of (8) is not known but data show that a collisional process is relatively unimportant.

The conclusion is reached, therefore, that over 99% of the absorbing molecules at 3340 Å. go to the triplet state.²⁴ Since this is true, equation 15 becomes

$$1/Q_p = \frac{(k_{10} + k_{11} + k_{12} + k_{11}'(\text{M}))}{k_{10}} \quad (16)$$

where k_{11}' is the constant for collisional deactivation.

Empirically the data in Fig. 3 show

$$1/Q_p = 630 + 5.3 P_{\text{AcH}} \quad (17)$$

where P_{AcH} is the pressure of acetaldehyde in mm. Thus at 30°, $k_{11}'/k_{10} = 1.0 \times 10^8$ ml. mole⁻¹ and $(k_{11} + k_{12})/k_{10} = 640$. The estimates of Calvert, *et al.*,²⁵ that at 3130 Å. $\phi_3 + \phi_4 + \phi_{12}$ reaches a limiting value of about 0.8 at temperatures above 250° indicates that (11) or (11') competes effectively with (12) even at high temperatures. Since no way exists to determine the absolute magnitude of (12), the magnitude of the intersystem cross-over to the ground state is not known.

(b) 3130 Å.—At 3130 Å. there is some dissociation by (1b) even in the presence of considerable nitric oxide. Also iodine does not suppress dissociation completely. In agreement with the work of Blacet, *et al.*,⁵ it may be assumed that (1a) and (1b) occur simultaneously and that (1b) increases relatively in importance at short wave lengths.

In the present work the yield of methane in the presence of nitric oxide is much lower than that found by Blacet, *et al.*, in the presence of iodine. Since iodine may have a deactivating effect on singlet as well as on triplet molecules, the value obtained by Blacet, *et al.*, should be a minimum. The discrepancy probably is due to the wave length distributions of the light sources.

At 3130 Å.

$$P_{\text{AcH}}/Q_f = 10300 + 547 P_{\text{AcH}} \quad (18)$$

Thus when $1/P_{\text{AcH}} = 0$, $1/Q_f = 547$, $Q_f = 1.8 \times 10^{-3}$. Equation 18 shows that (14) is obeyed provided either $k_8(\text{M})$ or $k_5(\text{M})$ is negligible. Actually the data at 3340 Å. show the singlet emission efficiency to be independent of pressure. Thus (8) is either first order or non-existent. If (8) is neglected (14) becomes

$$\frac{(\text{M})}{Q_f} = \frac{k_4(k_6 + k_7)}{k_5(1 - \phi_3)k_6} + \frac{k_8(k_6 + k_7)(\text{M})}{k_5(1 - \phi_3)k_6} \quad (19)$$

(23) K. K. Innes and L. E. Giddings, Jr., *J. Mol. Spectry.*, **7**, 435 (1961).

(24) See H. Ishikawa and W. A. Noyes, Jr., *J. Chem. Phys.*, **37**, 583 (1962), and W. A. Noyes, Jr., W. A. Mulac and M. S. Matheson, *ibid.*, **36**, 880 (1962).

(25) J. G. Calvert, J. N. Pitts and D. D. Thompson, *J. Am. Chem. Soc.*, **78**, 4239 (1956).

Thus dividing slope by intercept (Fig. 3) and converting to the proper units gives k_5/k_4 . Murad⁷ has shown this form of relationship to be valid also at 3020 and 2970 Å. $k_5/k_4 = 1.03 \times 10^6$ ml. mole⁻¹. The data do not permit the evaluation of k_5 and k_4 independently.

If the singlet emission efficiency at 3130 Å., 200 mm. pressure, is 1.63×10^{-3} , ϕ_3 is found to be 0.17.

From equation 19 and with the realization that $\phi_3 = 0$ at 3340 Å. one may state

$$\begin{aligned} \lim_{P_{\text{AcH}} \rightarrow 0} Q_i^{3130}/Q_i^{3340} &= (1 - \phi_3) \\ \frac{1.80 \times 10^{-3}}{2.14 \times 10^{-3}} &= 0.84 \\ \phi_3 &= 0.16 \end{aligned}$$

It should be noted that the sum of quantum yields of methane and methyl iodide in Blacet's work⁵ should be ϕ^I provided iodine does not deactivate the singlet state at the pressures used. This is almost certain to be true. This sum is about 0.2. If one calculated ϕ_4 from the rate constants at 200 mm. pressure, one obtains 0.07. Thus the total primary yield from the singlet state should be about 0.23 in satisfactory agreement with Blacet's work.

(c) 2537 Å.—At 2537 Å. emission from acetaldehyde is extremely weak but it is definitely not zero. Little can be deduced from this fact except that $\phi_3 + \phi_4$ must be nearly unity.

The quantum yield of methane formation in the presence of 12 or more millimeters of nitric oxide is about 0.65 and is somewhat pressure dependent but temperature independent. In Blacet's⁵ work, iodine suppresses about one-half of the methane formation. Blacet's methyl iodide yield is about 0.38, independent of temperature. Pressure dependence was not studied. Thus

the primary yield is about unity and comes entirely from the singlet state at this wave length.

One may conclude, therefore, that iodine suppresses part but not all of the non-free radical methane formation and does not suppress radical formation by (1a). The radical formation is presumably all by (3).

One could speculate on the kind of intermediate complex which would lead to non-free radical methane and carbon monoxide formation. The change in enthalpy for



is small. Methane behaves in many ways as an inert gas so that one would expect a repulsion between the two product molecules. Insertion of the aldehyde hydrogen between the two carbon atoms by a combination of carbon-carbon stretching and carbon-hydrogen bending motions might lead to the right result. Unfortunately there is little one can deduce from the spectrum along these lines. One may make the following statements:

1. At all wave lengths emission is a minor means of energy dissipation in acetaldehyde.
2. Dissociation at 3340 Å. must be mainly if not exclusively from the triplet state. Triplet emission at this wave length is only about one-third the intensity of the singlet emission.
3. Dissociation at 3130 Å. arises apparently from two sources: (a) a rapid process possibly arising from an upper repulsive state; (b) a somewhat slower process from vibrationally excited singlet state molecules. There is also some temperature dependent triplet dissociation at this wave length.
4. Dissociation at 2537 Å. must occur almost exclusively from the singlet state and emission is very weak.

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The Electroreduction of Quaternary Ammonium Compounds¹

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The electroreduction of anilinium chloride (AC), dimethylanilinium chloride (DMAC) and benzyldimethylanilinium bromide (BDAB) was studied polarographically and coulometrically. Analysis for the reduction products was performed spectrophotometrically. Application of Koutecký's treatment for irreversible polarographic waves indicated that all of the reductions involved a one-electron rate-determining step. Coulometry of AC and DMAC showed that one electron was also consumed in the over-all reaction. For BDAB, however, the apparent number of faradays per mole, n_{app}^0 , for the coulometric reduction in water, acetonitrile and N,N-dimethylformamide varied between 1.4 and 2.0. A mechanism for this reduction involving primary formation of a benzyl free radical, which either reacts with the solvent or couples, is proposed. Reduction of BDAB in the microwave cavity of an electron paramagnetic resonance spectrometer provides further evidence of a free radical intermediate.

The mechanism of the electroreduction of quaternary ammonium compounds has been the subject of several recent studies. Finkelstein, Peterson and Ross³ carried out uncontrolled, macroelectrolyses of several substituted anilinium salts at platinum and aluminum cathodes. Southworth, Osteryoung, Fleischer and Nachod⁴ recently reviewed the past literature and examined the polarographic and macroelectrolytic reduction of a number of aliphatic and aromatic quaternary ammonium compounds. Both groups, on the

basis of the nature of the products obtained, postulated an initial one-electron electrode reaction. Definitive electrochemical evidence for this reaction scheme was lacking, however. The present study was undertaken to obtain this evidence and to apply controlled potential coulometry, a technique which has proved very useful for the elucidation of electrode mechanisms,⁵ to a study of this reaction. Substituted anilinium compounds, which produce the best-defined polarographic waves and reduce well before the discharge of the supporting electrolyte, were chosen as model compounds in this study.

Results and Discussion

Polarography.—Well defined, irreversible, polarographic waves were obtained for the reduction of ani-

(1) (a) Based on a thesis submitted by J. S. Mayell in partial fulfillment of the requirements for the degree of Ph.D., June, 1962. (b) Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

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(3) M. Finkelstein, R. C. Peterson and S. D. Ross, *J. Am. Chem. Soc.*, **81**, 2361 (1959); **82**, 1582 (1960).

(4) B. C. Southworth, R. Osteryoung, K. D. Fleischer and F. C. Nachod, *Anal. Chem.*, **33**, 208 (1961).

(5) (a) D. H. Geske and A. J. Bard, *J. Phys. Chem.*, **63**, 1057 (1959); D. H. Geske, *ibid.*, **63**, 1062 (1959); (b) S. Karp and L. Meites, *J. Am. Chem. Soc.*, **84**, 906 (1962).