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New Mechanism of Photodissociation of Gaseous Acetone

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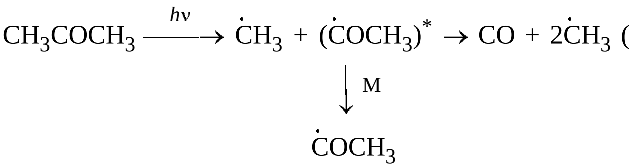
Abstract—It is found for the first time that photolysis of gaseous acetone under UV irradiation produces ethane not only via recombination of methyl radicals, but also by the mechanism of induced predissociation.

Photolysis of acetone is a well-understood photochemical process [1]. Gaseous acetone is even called a classical actinometric system [2]. Actually, it is firmly established [2] that at $T \geq 398$ K in a wide range of near-UV wavelengths (250–320 nm) the quantum yield of CO (φ_{CO}) formed by photolysis of gaseous acetone is exactly one [schemes (1) and (2)].

$$CH_3COCH_3 \xrightarrow{h\nu} CO + 2\dot{C}H_3, \qquad (1)$$

$$2\dot{C}H_3 \xrightarrow{k_2} C_2H_6. \qquad (2)$$

At lower temperatures at λ 313 nm, along with photodissociation (1), a less profound decomposition (3) becomes a significant pathway.



$$CH_3COCH_3 \xrightarrow{h\nu} \dot{C}H_3 + (\dot{C}OCH_3)^* \rightarrow CO + 2\dot{C}H_3 \qquad (3)$$
$$(\dot{C}OCH_3)^* \xrightarrow{M} \dot{C}OCH_3$$

Here M is the deactivating valence-saturated molecule, $(\dot{C}OCH_3)^*$ is the excited radical with increased vibrational temperature, which decomposes into CO and $\dot{C}H_3$ if M has no time to deactivate it. The $\dot{C}H_3$ radicals formed by reaction (3) recombine by scheme (2), as well as by schemes (4) and (5).

$$\dot{C}OCH_3 + \dot{C}H_3 \longrightarrow CH_3COCH_3, \qquad (4)$$

$$\dot{C}OCH_3 + \dot{C}OCH_3 \longrightarrow (CH_3CO)_2. \qquad (5)$$

According to [3], even a vibrationally deactivated radical $\dot{C}H_3CO$ is quite unstable and decomposes by scheme (6) similar by scheme (3) with a rate constant defined by Eq. (7).

$$\dot{C}H_3CO \longrightarrow \dot{C}H_3 + CO, \qquad (6)$$

$$k_6 = 1.25 \times 10^{10} \exp\left(-\frac{6740}{T/K}\right), \text{s}^{-1}. \qquad (7)$$

As follows from Eq. (7), the average time of the decomposition of $CH_3\dot{C}O$ by scheme (6) at 333 K is as short as 0.045 s.

Clearly, if pathway (3) is realized, the quantum yield φ_{CO} proves to be slightly lower than one, but the quantum yield of methyl radicals ($\varphi_{\dot{C}H_3}$) is always no less than double φ_{CO} [Eq. (8)].

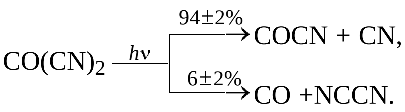
$$\varphi_{\dot{C}H_3} \geq 2\varphi_{CO}. \qquad (8)$$

Since gaseous acetone in photolytic kinetic studies serves as a source of free methyl radicals, relation (8) is a corner stone of gas-phase kinetics [3], allowing one to estimate the initial concentration $[\dot{C}H_3]_0$.

Whereas the above pattern seems quite clear, the mechanism of photolysis of gaseous acetone cannot be considered firmly established. The case in point is that, according to our data, mild pyrolysis (500–600 K) of gaseous methyl iodide gives no ethane. We also found that no ethane is also formed by photolysis of methyl iodide. These findings led us to suggest that the ethane resulting from photolysis of acetone is mostly formed by induced predissociation (9) rather than by recombination (2).

$$CH_3COCH_3 \xrightarrow{h\nu} C_2H_6 + CO. \qquad (9)$$

Actually, some evidence for this mechanism could be found in experiments with hard irradiation at $\lambda \leq 200$ nm [3]. Recently, Scheld *et al.* [4] used the molecular-beam technique to show that photodissociation of carbocyanide (λ 193 nm) gives dicyan by the intramolecular predissociation mechanism [scheme (10)] with a probability of 6%.



$$CO(CN)_2 \xrightarrow{h\nu} \begin{cases} \xrightarrow{94\pm2\%} COCN + CN, \\ \xrightarrow{6\pm2\%} CO + NCCN. \end{cases} \qquad (10)$$

Thus, instead of photodissociation of gaseous

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acetone [schemes (1)–(3)], we can propose a more general scheme of photodissociation of any two-ligand carbonyls:

$$R^1COR^2 \begin{cases} \xrightarrow{\varphi^0} R^1COR^2 \text{ (stabilization)}, \\ \xrightarrow{\varphi^1} \dot{R}^1 + \dot{R}^2 + CO, \\ \xrightarrow{\varphi^2} \dot{R}^1 + \dot{R}^2CO, \\ \xrightarrow{\varphi^3} \dot{R}^2 + \dot{R}^1CO, \\ \xrightarrow{\varphi^4} R^1R^2 + CO, \\ \xrightarrow{\varphi^5} \text{Isomerization} \end{cases} \qquad (11)$$

For example, the φ^4 values for formaldehyde (R^1 = H, R^2 = H) range from 0.17 (λ 355 nm) to 0.65 (λ 280 nm) [5].

Thus, mechanism (9) as a possible way of ethane formation in in photolysis of gaseous acetone ethane seems quite reasonable. In the present work we experimentally measured quantum yields φ^4 for acetone.

To reveal pathway *4* in photodissociation (11) and to measure quantum yield φ^4, experiments with molecular beams are unnecessary. The same result can be obtained using a multilabeled compound [6], i.e. with a compound containing isotopic molecules in extremely nonequilibrium concentrations. Thus, the fully deuterated analog $(CD_3)_2CO$ is similar to acetone in photochemical properties [1]. The free radicals $\dot{C}D_3$ recombine by scheme (12) with an almost the same rate constant [7] as their protium analogs [Eq. (13)].

$$\dot{C}D_3 + \dot{C}D_3 \xrightarrow{k_{12}} C_2D_6, \qquad (12)$$

$$k_{12}/k_2 = (15/18)^{1/2} = 0.913. \qquad (13)$$

Therefore, in photolysis of a multilabeled acetone, i.e. to a mixture of $(CH_3)_2CO$ and $(CD_3)_2CO$, predissociative channel *4* will lead to exclusive formation of C_2H_6 and C_2D_6. By contrast, dissociative channels *1* and *2* will three species: C_2H_6, C_2D_6, and $C_2H_3D_3$, whose fractions are quite accurately determined [6] by combinatorial formulas (14).

$$[C_2H_6] = 1/2x_0^2,\ [C_2H_3D_3] = x_0y_0,\ [C_2D_6] = 1/2y_0^2. \qquad (14)$$

Here x_0 is the molar fraction of initial radicals $\dot{C}H_3$ and $y_0 = 1 - x_0$ is the molar fraction of initial radicals $\dot{C}D_3$. Thus, the entire excess of C_2H_6 and C_2D_6 molecules in the photolytically formed ethane over those expected by formula (14) will give arise by channel *4* in scheme (11).

Table 1 represents the isotopic composition of the ethane formed by photolysis of deuteroacetone and the calculated fraction of the molecules formed by predissociative mechanism (9). It proved that this fraction is independent of the pressure and temperature of photolyzed acetone and is $\varphi^4 = 0.263 \pm 0.017$.

Strictly speaking, any difference in the rates of recombinations (2) and (12) should decrease the yield of $C_2H_3D_3$ at the expence of increased yields of C_2H_6 and C_2D_6. In this case, φ^4 should decrease correspondingly.

Let us consider a formal-kinetical problem of recombination of two components of the same kind [Eqs. (15)].

$$\begin{aligned} X + X &\xrightarrow{k_{X_2}} X_2, \\ X + Y &\xrightarrow{k_{XY}} XY, \\ Y + Y &\xrightarrow{k_{Y_2}} Y_2. \end{aligned} \qquad (15)$$

Reactions (15) have kinetic equations (16) and (17).

$$\begin{aligned} -dx/dt &= 2k_{X_2}x^2 + k_{XY}xy \\ -dy/dt &= 2k_{Y_2}y^2 + k_{XY}xy. \end{aligned} \qquad (16)$$

$$\begin{aligned} [X_2] = k_{X_2}\int_0^t x^2dt,\ [XY] &= k_{YY}\int_0^t xydt, \\ [Y_2] = k_{Y_2}\int_0^t y^2dt. \end{aligned} \qquad (17)$$

Here *x* is the concentration [X] and *y* is the concentration [Y]. Equations (16) has been solved in [8]. In particular, if the rate constants are related by Eq. (18), substitution of the solution of Eqs. (16) into Eq. (17) gives Eqs. (19) for the concentration of recombination products.

$$k_{X_2}\ 1/2k_{XY} = k_{Y_2} = k, \qquad (18)$$

$$\left.\begin{aligned} [X_2]_t &= \frac{x_0^2}{2}\left(1 - \frac{1}{1 + 2kt}\right), \\ [XY]_t &= x_0y_0\left(1 - \frac{1}{1 + 2kt}\right), \\ [Y_2]_t &= \frac{y_0^2}{2}\left(1 - \frac{1}{1 + 2kt}\right). \end{aligned}\right\} \qquad (19)$$

Here x_0 in the initial molar concentration $[X]_0$ and y_0 is the initial molar concentration $[Y]_0$, and $x_0 + y_0 = 1$. In particular, at $t \to \infty$, from Eqs. (19) follow Eqs. (20).

Table 1. Calculation of the fraction of the ethane formed by induced predissociation of photolyzed acetone (9)

$[\text{Acetone}]_0$, molecules/cm^3	Isotopic molecule	Measured isotopic composition of ethane, molar fraction	Calculated of recombination of CH_3 and CD_3, molar fraction[a]	Contribution predissociation (9), molar fraction	Ethane formed intramolecularly, %
9.7×10^{17} [b]	CH_3CH_3	0.477 ± 0.001	0.3065	0.170 ± 0.002	26.3 ± 0.4
	CH_3CD_3	0.337 ± 0.001	0.3373	0	
	CD_3CD_3	0.186 ± 0.001	0.0928	0.093 ± 0.002	
3.9×10^{18} [b]	CH_3CH_3	0.487 ± 0.009	0.3265	0.161 ± 0.015	24.5 ± 2.4
	CH_3CD_3	0.340 ± 0.008	0.3402	0	
	CD_3CD_3	0.173 ± 0.008	0.0886	0.084 ± 0.009	
3.9×10^{18} [c]	CH_3CH_3	0.360 ± 0.001	0.2088	0.151 ± 0.002	28.1 ± 0.4
	CH_3CD_3	0.357 ± 0.001	0.3573	0	
	CD_3CD_3	0.283 ± 0.001	0.1528	0.130 ± 0.002	

[a] Calculated by combinatorial formulas [6] without account for isotopic effects. [b] Temperature of photolyzed gas 340 K. [c] Photolysis temperature 418–438 K.

$$[X_2]_\infty = 1/2x_0^2,\quad [XY]_\infty = x_0y_0,\quad [Y_2]_\infty = 1/2y_0^2. \tag{20}$$

As seen from Eqs. (19) and (20), in recombination (15) of components X and Y, which have the same reactivity [see Eq. (18)], recombination products are formed in quantities calculated by combinatorial formulas [6].

Let us consider the other limiting case, when the rate constants of reaction (15) are strongly different [Eq. (21)].

$$k_{X_2} >> k_{Y_2},\quad k_{XY} = 2(k_{X_2}k_{Y_2})^{1/2}. \tag{21}$$

With the denotations $\tau = 2k_{X_2}t$ and $\alpha = k_{Y_2}/k_{X_2}$, Eqs. (16) can be rewritten to obtain Eqs. (22).

$$\begin{aligned} -\,dx/d\tau &= x^2 + \alpha^{1/2}xy \\ -\,dy/d\tau &= \alpha y^2 + \alpha^{1/2}xy. \end{aligned} \tag{22}$$

In force of conditions (21), we have $\alpha << 1$; as a result, the solution of Eqs. (22) can be written, to a high accuracy, in form (23).

$$x = \alpha^{1/2}y_0\left[\left(1 + \alpha^{1/2}\frac{y_0}{x_0}\right)e^{\alpha^{1/2}y_0\tau} - 1\right]^{-1}. \tag{23}$$

Substitution of Eq. (23) into integrals (17) gives Eq. (24).

$$[X_2]_t = \alpha^{1/2}y_0\left[\ln\frac{z - 1/(1+\alpha^{1/2}y_0/x_0)}{z} + \frac{z}{z - 1/(1+\alpha^{1/2}y_0/x_0)}\right]_{z = \exp(2\alpha^{1/2}y_0k_{X_2}t}^{z=1} \tag{24}$$

For $t \to$, from Eq. (24) we obtain Eq. (25).

$$[X_2]_\infty = \frac{x_0}{2} + \frac{\alpha^{1/2}}{2}(1 - x_0)\ln\frac{\alpha^{1/2}y_0/x_0}{1 + \alpha^{1/2}y_0/x_0}. \tag{25}$$

In particular, for $x_0 = y_0 = 0.5$, from Eq. (25) follows Eq. (26).

$$[X_2]_\infty = 1/4\left(1 + \alpha^{1/2}\ln\frac{\alpha^{1/2}}{1 + \alpha^{1/2}}\right). \tag{26}$$

Therewith, Eqs. (27) are valid.

$$[Y_2]_\infty = [X_2]_\infty,\quad [XY]_\infty = 1 - 2[X_2]_\infty. \tag{27}$$

Table 2 represents the final distributions of products of recombination (15), calculated by formulas (26) and (27) with varied values of $\alpha = k_{Y_2}/k_{X_2}$, as well as the final distribution for $\alpha = 0.913$, corresponding to the ratio of the rate constants of recombination of the radicals $\dot{C}D_3$ and $\dot{C}H_3$. As seen from Table 2, the kinetic isotope effect in recombination of the mixture $\dot{C}D_3 + \dot{C}H_3$ increases [compared with that expected by combinatorial formulas (20)] the molar fraction of the molecules C_2H_6 and C_2D_6 by about 0.2%. Allowance for this isotope effect gives a more accurate estimate for φ^4 (0.26 ± 0.02 instead of 0.263 ± 0.017).

Table 2. Composition of final products of recombination (15) at $[X]_0 = [Y]_0 = 0.5$ for $k_{XY} = 2(k_{X_2}k_{Y_2})^{1/2}$

k_{Y_2}/k_{X_2}	Final concentrations of recombination products, molar fraction[a]		
	$[X_2]_\infty$	$[XY]_\infty$	$[Y_2]_\infty$
10^{-6}	0.496546	0.006909	0.496546
10^{-4}	0.476925	0.046150	0.476925
10^{-2}	0.3801	0.2398	0.3801
10^{-1}	0.2745	0.4510	0.2745
0.913[b]	0.2521[c]	0.4957[c]	0.2521
1	0.25[d]	0.50[d]	0.25[d]

[a] Calculated by formulas (26) and (27). [b] Corresponds to the ratio $k_{C_2D_6}/k_{C_2H_6}$ [see Eq. (13)]. [c] Obtained by interpolation. [d] Calculated by Eqs. (20).

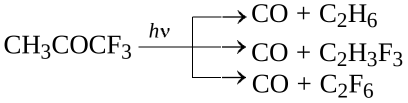
Table 3. Quantum yields (φ^4) of the intramolecular route of formation of product R^1R^2 on photolysis of oxo compounds R^1COR^2 or azomethanes $R^1N{=}NR^2$

Fotolized gas	Temperature, K	Irradiation wavelength, nm	φ^4	Reference
HCOH	300	280	0.65	[5]
		297	0.50	
		316	0.33	
		340	0.20	
		355	0.17	
DCOD	300	280	0.72	[5]
		297	0.57	
		316	0.33	
		340	0.20	
		355	0.17	
CH_3COCH_3	340	300–360	0.26 ± 0.02	[a]
CH_3COCF_3	420–470	313	0.11 ± 0.02	[9]
NCCOCN	300	193	0.06 ± 0.02	[4]
$F_3CN{=}NCH_3$	300	350–380	0.12 ± 0.01	[10]

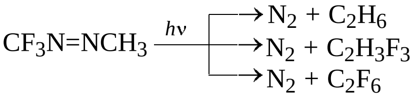
[a] Present work.

The resulting φ^4 value for the nondissociative channel of ethane formation in photolysis of gaseous acetone proved to be rather high. But its comparison with the φ^4 values for HCOH and NC–CO–CN (Table 3) shows that acetone is a usual carbonyl compound in terms of this property.

In connection with the aforesaid, a question arises as to whether photolysis of other oxo compounds and their azomethane analogs involve channel *4*. The compositions of final products of photolysis of methyl trifluoromethyl ketone and trifluoroazomethane have been reported in [9, 10].



$$CH_3COCF_3 \xrightarrow{h\nu} \begin{cases} CO + C_2H_6 \\ CO + C_2H_3F_3 \\ CO + C_2F_6 \end{cases}$$



$$CF_3N{=}NCH_3 \xrightarrow{h\nu} \begin{cases} N_2 + C_2H_6 \\ N_2 + C_2H_3F_3 \\ N_2 + C_2F_6 \end{cases}$$

By comparing the actual distribution [10, 11] of final products (C_2H_6, $C_2H_3F_3$, C_2F_6) with that predicted by combinatorial equations (20) we could estimate quantum yields φ^4 for both cases (Table 3). Here, too, the φ^4 values proved to be appreciably higher than zero. Data in Table 3 reveal a general regularity: The quantum yield φ^4 in process (11) decreases with increasing size of substituents R^1 and R^2.

EXPERIMENTAL

The isotopic mixtures with the molar compositions 64.4 mol% $(CH_3)_2CO$ + 35.6 mol% $(CD_3)_2CO$ and 53.8 mol% $(CH_3)_2CO$ + 46.2 mol% $(CD_3)_2CO$ were prepared gravimetrically.

A mixture, 1 g, was placed into the ampule of a vacuum device, purified by triple vacuum distillation, and dried for 2 h over 4 Å + 5 Å Zeolites preheated in a vacuum. The purified mixture was transferred in a vacuum into 4 quartz photolytic cells. Each of the cells was irradiated for 30 min with a medium-pressure mercury lamp (the first and second at 70°C, the third at 140°C, and the fourth at 165°C). After photolysis, the cells were attached to the inlet probe of an MKh-1321 mass spectrometer, and the isotopic compositions of ethane were measured at an ionizing voltage of 70 V. The mass spectra were assigned using the databases [11, 12].

The mass spectral results for ampules 1 and 2 are listed in Table 4. The last column in the table represents the isotopic compositions of hydrogen, which coincide, within error, with the more exact isotopic composition obtained gravimetrically. These results show that the mass spectral analysis and the assignment of the mass spectra are correct. The same checking procedure was performed for ampules 3 and 4. Data in Table 4 were used for constructing Table 1.

ACKNOWLEDGMENTS

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Table 4. Isotopic compositions of the ethane formed by photolysis (λ > 300 nm, T 340 K) of a gaseous mixture containing 64.4 mol% $(CH_3)_2CO$ and 35.6 mol% $(CD_3)_2CO$[a]

$[\text{Acetone}]_0$, molecules/cm^3	Reaction product	Mass number	Relative intensity [11][a]	Isotopic composition of ethane		Isotopic composition of hydrogen in ethane	
				measured intensity rel. units	molar concentration, %	atom	atomic fraction
9.7×10^{17}	CH_3CH_3	27[b]	33 ± 1	190 ± 5	47.7 ± 2.8	H	0.645 ± 0.041
	CH_3CD_3	33	27 ± 5	110 ± 5	33.7 ± 2.6		
	CD_3CD_3	36	20	45 ± 5	18.6 ± 1.2	D	0.335 ± 0.025
3.9×10^{18}	CH_3CH_3	27	33 ± 1	70 ± 5	48.7 ± 4.3	H	0.657 ± 0.063
	CH_3CD_3	33	27 ± 1	40 ± 3	34.0 ± 4.0		
	CD_3CD_3	36	20	15 ± 1	17.3 ± 1.1	D	0.343 ± 0.031

[a] Measured at an ionizing energy of 50–70 eV [11]. [b] The molecular ion peak (*m/e* 30) was not used, since it is contributed by tri- and hexadeuteroethanes.

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