

SENSITIVE CHEMICAL ACTINOMETRY WITH ACETONE-HYDROGEN CHLORIDE MIXTURES

ABRAHAM HOROWITZ

Department of Radiation Chemistry, Soreq Nuclear Research Center, Yavne 70600 (Israel)

(Received August 21, 1986; in revised form October 27, 1986)

Summary

The 2850, 3000 and 3130 Å photolysis of acetone-hydrogen chloride mixtures was studied at 130 °C. The effect of HCl pressure (1 - 8 Torr), CH₃COCH₃ pressure (5 - 60 Torr) and incident light intensity on the formation of CO and CH₄ was examined. Under the conditions employed, methyl radicals are completely scavenged by HCl and $\Phi_{\text{CH}_4}/\Phi_{\text{CO}} = 2$. Based on this finding and the availability of sensitive techniques for CH₄ detection, it is suggested that the CH₃COCH₃-HCl system can be used as a convenient and sensitive chemical actinometer. The potential advantages and applications of this method are discussed.

1. Introduction

The photochemistry of acetone has been extensively studied for more than 50 years [1 - 4]. As a result of these studies, the mechanism of CH₃COCH₃ photodissociation and its wavelength, pressure and temperature dependence are known. At temperatures exceeding about 120 °C at all wavelengths corresponding to the π^* -n transition and at pressures below 50 Torr, CH₃COCH₃ undergoes photodissociation by the following reactions:



The quantum yield of decomposition is unity and hence $\Phi_{\text{CO}} = 1$. Based on this observation and the absence of fine structure in the absorption spectrum, gaseous CH₃COCH₃ has been widely used as a chemical actinometer, and is similar to azomethane in its applications and sensitivity [5].

The use of CH₃COCH₃ as a chemical actinometer requires an accurate and sensitive method of CO analysis. This is usually carried out gas chromatographically employing thermal conductivity (TC) detectors. CH₄ can be detected with flame ionization (FI) detectors, which are at least three orders of magnitude more sensitive to CH₄ than TC detectors are to CO.

Therefore, it is evident that the sensitivity of CH_3COCH_3 as a chemical actinometer could be considerably increased provided that a method could be found whereby the initially formed methyl radicals would be quantitatively converted into CH_4 . As early as 1953 Cvetanovic and Steacie [6] showed that the addition of 1 Torr HCl to 100 Torr CH_3COCH_3 , on photolysis at room temperature and at 150 °C, resulted in complete conversion of methyl radicals to CH_4 . For a long time these findings were overlooked and their potential application was not realized. However, recently it has been shown in this laboratory that the addition of HCl allows the methyl radicals formed in the photodecomposition of acetaldehyde to be determined accurately [7]. In the light of these findings and the results of Cvetanovic and Steacie, the present investigation was initiated in an attempt to examine the potential advantages of the CH_3COCH_3 -HCl system as a convenient chemical actinometer.

2. Experimental details

CH_3COCH_3 (Biolab, AnalaR) was dried over potassium carbonate and HCl (Matheson) was degassed and purified by trap-to-trap distillation.

The 130 °C photolysis was carried out in a cylindrical quartz cell (length, 21.6 cm; internal diameter, 4.6 cm) placed in an air-heated oven in which the temperature was regulated to within ± 0.5 °C. The light from an Osram HBO 200 W lamp at the different wavelengths was isolated with a high intensity grating monochromator (Schoeffel GM 252) and was attenuated when necessary with neutral density filters. Slits were set at 2 mm, giving an effective half-bandwidth of 66 Å. Half the cell volume ($V = 370 \text{ cm}^3$) was illuminated and the light transmitted through it was monitored with an RCA 935 photodiode mounted at the rear of the cell and connected to an Oriel model 7072 detection system coupled with a data logging system. The product gases were Toepler pumped through two traps held at liquid N_2 temperature. Gases that did not condense at this temperature were transferred to a precalibrated volume in which their total pressure was measured. At low conversions only CH_4 was determined with an FI detector. In other runs, in which simultaneous determination of CO and CH_4 was carried out, a flow splitter was introduced at the end of the gas chromatography (GC) column. With this splitter, 90% of the sample volume was directed to the TC detector and the remainder to the FI detector. A molecular sieve 5A column (1/8 in \times 8 ft) was used for the GC analysis. Absolute intensities were estimated by taking $\Phi_{\text{CO}} = 1$ in CH_3COCH_3 .

3. Results

The main objective of the present study was to establish the potential advantages of the CH_3COCH_3 -HCl system as a chemical actinometer. The

formation of CO and CH₄ was studied in considerable detail at 3130 Å as a function of time, HCl and CH₃COCH₃ pressure and incident light intensity. The results of these experiments are presented in Figs. 1 - 4. The least-squares-computed expressions for the time dependence lines shown in Fig. 1 are

$$[\text{CH}_4] (\times 10^{-9} \text{ mol l}^{-1}) = (3.5 \pm 6.0) + (1.31 \pm 0.03)t \quad \text{where } t \text{ is in seconds}$$

$$[\text{CO}] (\times 10^{-9} \text{ mol l}^{-1}) = (5 \pm 10) + (0.65 \pm 0.006)t \quad \text{where } t \text{ is in seconds}$$

indicating that at up to 0.5% CH₃COCH₃ conversion the formation of these products is independent of time. In other words, secondary reactions do not interfere with the primary photodecomposition reactions. A linear dependence between the rates of formation and the incident line intensity can be seen from the plot shown in Fig. 2. In this case the slope and the intercept of the line are 0.97 ± 0.08 and 0.017 ± 0.04 respectively. From Fig. 3 it can be seen that the rates of formation of CO and CH₄ are independent of HCl pressure (1 - 8 Torr). Furthermore, as shown in Fig. 4, the ratio of the rates at which these two products are formed is constant (2.00 ± 0.08) throughout the CH₃COCH₃ pressure range of 5 - 60 Torr.

Additional experiments were carried out at 2850 and 3000 Å, all at a CH₃COCH₃ pressure of 50 Torr. The results of these experiments, as well as of those at 3130 Å, are summarized in Table 1.

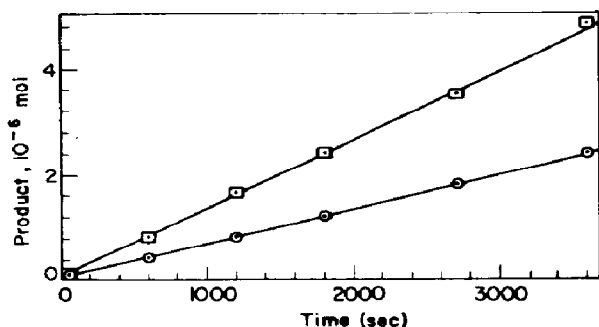


Fig. 1. Time dependence of CH₄ (squares) and CO (circles) formation at 3130 Å. $I_0 = 1.03 \times 10^{13}$ quanta $\text{cm}^{-3} \text{s}^{-1}$, $P_{\text{CH}_3\text{COCH}_3} = 50$ Torr and $P_{\text{HCl}} = 2$ Torr.

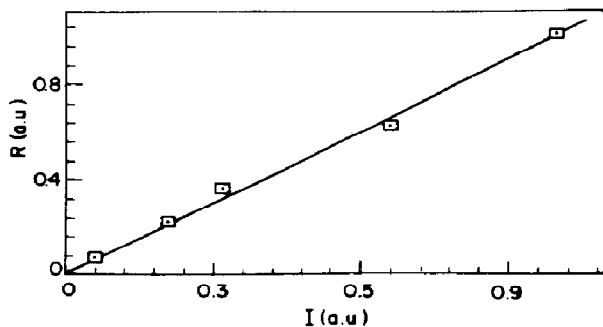


Fig. 2. Variation in R_{CH_4} with incident light intensity at 3130 Å. $\Phi_{\text{CO}} = 1$ and $R_{\text{CH}_4} = 1$ at $I_0 = 1 \times 10^{13}$ quanta $\text{cm}^{-3} \text{s}^{-1}$. $P_{\text{CH}_3\text{COCH}_3} = 50$ Torr and $P_{\text{HCl}} = 2$ Torr.

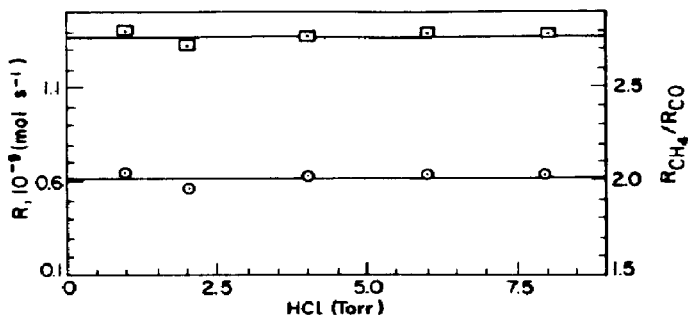


Fig. 3. Effect of HCl pressure on the rate of formation of CH_4 (squares) and $R_{\text{CH}_4}/R_{\text{CO}}$ (circles) at 3130 Å. $P_{\text{CH}_3\text{COCH}_3} = 50$ Torr and $I_0 = 0.95 \times 10^{13}$ quanta $\text{cm}^{-3} \text{s}^{-1}$.

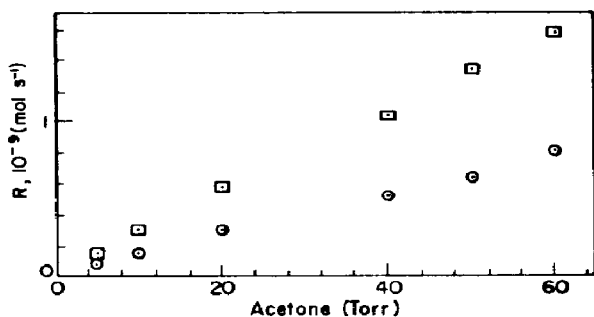


Fig. 4. Variation in R_{CH_4} (squares) and R_{CO} (circles) with CH_3COCH_3 pressure at 3130 Å. $P_{\text{HCl}} = 2$ Torr, normalized to $I_0 = 1 \times 10^{13}$ quanta $\text{cm}^{-3} \text{s}^{-1}$.

TABLE 1

CH_4 and CO formation in the photolysis of CH_3COCH_3 -HCl mixtures at 130 °C

λ (Å)	Number of runs	P_{acetone} (torr)	P_{HCl} (torr)	I_a^{1a} ($\times 10^{12}$ quanta $\text{cm}^{-3} \text{s}^{-1}$)	$[\text{CH}_4]/[\text{CO}]^b$	$P_{\text{NC}}/[\text{CH}_4]^c$
2850	10	50	2	1.5 ± 0.1	1.99 ± 0.05	1.52 ± 0.07
3000	12	50	2	7.0 ± 0.6	1.98 ± 0.06	1.49 ± 0.03
3130	31	5 - 60	1 - 8	0.6 - 10	2.02 ± 0.05	1.47 ± 0.06

^a Assuming $\Phi_{\text{CO}} = 1$.

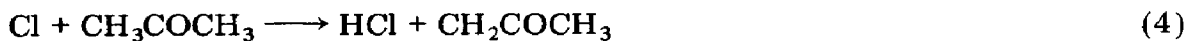
^b CH_4 and CO determined directly at 3130 Å, only ten runs.

^c NC, non-condensable gases at liquid N_2 temperature (all runs).

4. Discussion

4.1. Kinetic scheme and mechanism

At 130 °C all acetyl radicals formed in the primary photodissociation step decompose. Therefore, under our experimental conditions the occurrence of the following reactions should be considered:



In this reaction scheme radiative transitions of the excited CH_3COCH_3 molecules were neglected since even at 50 °C the sum of the quantum yields of fluorescence and phosphorescence is lower than 0.02 [8]. Thus, in the estimation of the incident light intensity throughout this work, it has been assumed that $\Phi_{\text{CO}} = 1$.

According to the present results, Φ_{CH_4} is independent of HCl pressure, indicating that all methyl radicals are scavenged by the HCl. In this case, reactions (5) and (6) need not be considered and material balance considerations lead to the following relation

$$R_{\text{CH}_4} = 2R_{\text{CO}} \quad (8)$$

Examination of the results summarized in Table 1 shows that this relation is indeed obeyed by our experimental findings. Furthermore, the ratio of the total pressure of the product gases which did not condense at liquid N_2 temperature to the pressure of methane was found to be 1.5, again in agreement with expression (8).

Finally it should be noted that, according to the suggested mechanism, scavenging of the methyl radicals does not result in depletion of HCl concentration since HCl is regenerated in reaction (4).

4.2. CH_3COCH_3 -HCl actinometry: scope and limitations

The present findings clearly demonstrate the applicability of the CH_3COCH_3 -HCl system as a sensitive chemical actinometer. In comparison with CH_3COCH_3 the only disadvantage of this system is its sensitivity to moisture and the need to handle two gaseous components instead of one. This can be considered a minor complication since, in any case, a vacuum gas handling system is required for CH_3COCH_3 actinometry.

This drawback of the CH_3COCH_3 -HCl system is more than offset by the enhanced sensitivity and versatility of this technique. Thus, CH_4 can be easily determined at the parts per million level, and therefore the gases formed in the irradiated volume can be directly sampled from it rather than having to be preconcentrated by transfer to a smaller volume. Alternatively, if such a transfer procedure is applied, in a leak-proof system, the actinometry can be estimated directly from the pressure of the liquid N_2 non-

condensable gases, taking $\Phi_{\text{PNC}} = 3$. In this case GC analysis can be completely avoided.

As a final note it should be emphasized that actinometry based on the use of $\text{CH}_3\text{COCH}_3\text{-HCl}$ mixtures cannot be used directly at very high intensities, such as those encountered in flash photolysis. The upper limit of the absorbed intensities at which this method can be used is determined by the rates of the termination reactions in which the methyl radicals are involved and those which compete with its removal via hydrogen abstraction reactions (2) and (3).

In a given $\text{CH}_3\text{COCH}_3\text{-HCl}$ mixture the fraction F of methyl radicals which are converted to methane is given by

$$F = \frac{R_2 + R_3}{R_2 + R_3 + 2R_5 + R_6}$$

$$= \frac{k_2[\text{HCl}] + k_3[\text{CH}_3\text{COCH}_3]}{k_2[\text{HCl}] + k_3[\text{CH}_3\text{COCH}_3] + 2k_5[\text{CH}_3] + k_6[\text{CH}_3\text{COCH}_2]} \quad (9)$$

For the purpose of an approximate estimation of the maximum intensity I_{max} , defined here as the intensity at which 99% of the methyl radicals are converted into CH_4 , it can be assumed that $k_5 = k_6$. Furthermore, the upper limit of methyl radical steady state concentration, and hence the lower limit of I_{max} , is derived when this concentration is obtained by equating the rate of initiation to the rate of termination by recombination of methyl radicals ($F = 0.99$, $\Phi_{\text{CH}_3} = 2$ and $I = 2k_5[\text{CH}_3]^2$).

$$I_{\text{max}} = \frac{10^{-4}(k_2[\text{HCl}] + k_3[\text{CH}_3\text{COCH}_3])^2 \times 6.023 \times 10^{20}}{4k_5} \text{ quanta cm}^{-3} \text{ s}^{-1} \quad (10)$$

For example, at 403 K, taking $k_2 = 1.32 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$, $k_3 = 6.68 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ from the evaluation of Kerr and Parsonage [9] and $k_5 = 3.25 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ estimated from the data of Macpherson *et al.* [10], I_{max} is found to be $3.5 \times 10^{15} \text{ quanta cm}^{-3} \text{ s}^{-1}$ at HCl and CH_3COCH_3 pressures of 5 Torr and 50 Torr respectively.

References

- 1 W. A. Noyes, Jr., G. B. Porter and J. E. Jolley, *Chem. Rev.*, **56** (1956) 49.
- 2 J. N. Pitts, Jr., and J. K. S. Wan, in S. Patai (ed.), *The Chemistry of the Carbonyl Group*, Wiley-Interscience, New York, 1966, p. 823.
- 3 E. K. C. Lee and R. S. Lewis, *Adv. Photochem.*, **12** (1980) 1.
- 4 A. J. C. Nicholson, *Can. J. Chem.*, **61** (1983) 1831.
- 5 J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, Wiley, New York, 1966, p. 782.
- 6 R. J. Cvetanovic and E. W. R. Steacie, *Can. J. Chem.*, **31** (1953) 158.
- 7 A. Horowitz, *J. Phys. Chem.*, **90** (1986) 4393.
- 8 R. B. Cundall and A. S. Davies, *Proc. R. Soc. London, Ser. A*, **290** (1966) 563.
- 9 J. A. Kerr and M. J. Parsonage, *Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals*, Butterworth, London, 1976.
- 10 M. T. Macpherson, M. J. Pilling and M. J. C. Smith, *J. Phys. Chem.*, **89** (1985) 2268.