solute with the surface caused by preferential binding could possibly give a wrong value for the nonfreezing water fraction. However, we have found at room temperature no difference between the EPR spectra of 0.10 M CuCl₂ solutions dispersed in S-G25 and nondispersed and therefore believe this effect to be negligible at low temperatures in the investigated disperse systems. Secondly, in the case of a highly concentrated CuCl₂ phase formed during freezing, the nonfreezing water fraction could be falsified by the formation of vitreous CuCl₂ solution which would behave just like the nonfreezing water fraction and give EPR spectra reversible with temperature without further ice formation (Figure 2D). This problem can be prevented by choosing the initial CuCl₂ concentrations such that after freezing solute concentrations of at most 2.5 M (Figure 4,B and C) are formed. At this concentration the nonfreezing water fraction shows no further tendency for ice formation at 243 K.

¹H NMR of water on S-G25 and CPG-50 gave data consistent with the EPR method. A better correlation between ¹H NMR and EPR data is not possible because the half-bandwidth of the ¹H NMR signal in nonfreezing water prevents the quantitative determination of a small nonfreezing water fraction as found, for example, in CPG-50 with EPR.

In samples with kinetic effects a distribution of CuCl₂ concentrations is present due to the high crystallization velocity of the solvent and therefore a more detailed evaluation of the various concentrations does not appear to be meaningful. On the other hand, in samples with nonfreezing water fractions it should be possible to generate a uniform CuCl₂ concentration by cooling very slowly and/or by prolonged annealing at temperatures only slightly below the melting point. A more exact determination of the CuCl₂ concentration via the concentration dependence of the half-bandwidth of the EPR signal is in progress. We believe this EPR method to be of great help in the study of nonfreezing water in other dispersed forms. membranes and possibly macromolecules. An application of the kinetic effect observed in w/o emulsions for estimating relative cooling rates has been reported already.¹⁵

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Kinetics of the Unimolecular Elimination of Chlorobutanones in the Gas Phase

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The gas-phase unimolecular elimination of 3-chloro-3-methyl-2-butanone has been investigated, in a static system and seasoned vessel, over the temperature range of 340–395 °C and the pressure range of 60–190 torr. The reaction is homogeneous and unimolecular, follows a first-order rate law, and is invariable in the presence of cyclohexane, a radical-chain inhibitor. The products are isopropenyl methyl ketone and hydrogen chloride. The rate coefficients are given by the Arrhenius equation log $k_1(s^{-1}) = (12.56 \pm 0.31) - (190.8 \pm 3.7)$ kJ mol⁻¹ $(2.303RT)^{-1}$. When primary, secondary, and tertiary chlorobutanones are compared the presence of acetyl at the C_g-Cl bond causes a significant rate enhancement due to the -M effect. However, if this substituent is at the C_g-Cl bond, deactivation in rate of elimination of these compounds is observed. The present work could well provide a general view on the effect of the acetyl substituent at the C_g-Cl bonds in the molecular elimination of haloketones in the gas phase.

Introduction

Two different effects have been attributed to the acetyl substituent in the pyrolysis rates of 3-chloro-2-butanone² and 4-chloro-2-butanone³ in the gas phase. The slow decomposition velocity of the former compound was explained in terms of the –I inductive withdrawal of the CH₃CO group, whereas an appreciable rate enhancement of the latter compound was thought to be due to the –M effect of the said CH₃CO group. Both considerations have provided additional evidence of the heterolytic nature of the transition state in alkyl halide pyrolyses.⁴ In view of the above results, it seemed interesting, therefore, to find whether any other factor may influence the gas-phase elimination of a tertiary chlorobutanone. In this sense, the present work was aimed at studying the effect on the

CH₃CO on a tertiary C–Cl bond in 3-chloro-3-methyl-2butanone. Furthermore, the previous reported kinetic parameters in addition to those to be found in this study may provide a general view of the effect of the acetyl substituent at the C_{α} –Cl and C_{β} –Cl bonds in molecular elimination of haloketones in the gas phase.

Experimental Section

3-Chloro-3-methyl-2-butanone (bp 105 °C at 620 torr) was prepared by the treatment of isopropyl methyl ketone with SO_2Cl_2 as reported.⁵ This halide substrate was distilled several times, and the fraction with 99.2% purity (gas-liquid chromatography) was used. Isopropenyl methyl ketone (K & K Labs) was also distilled until at least 99.0% pure and was used as standard reference. A column of FFAP-7% Chromosorb G AW DMCS 80-100 mesh was used for quantitative analysis of the substrate and the product. The identities of these compounds were addi-

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⁽²⁾ Dakubu, M.; Maccoll, A. J. Chem. Soc. B. 1969, 1248.

⁽³⁾ Dominguez, R. M.; Chuchani, G. Int. J. Chem. Kinet. 1981, 13, 403.
(4) Maccoll, A. Chem. Rev. 1969, 69, 33.

⁽⁵⁾ Wejman, D. P.; Kaufman, P. R. J. Org. Chem. 1964, 29, 1956.

TABLE I: Stoichiometry Based on the Ratio of Final to Initial Pressure

temp, °C	339.8	349.0	360.0	370.0	378.9	388.9	394.5
P_0 , torr	114	112	115	78	102	77	59
P_{f} , torr	227	222	227	254	205	258	119
P_{f}/P_{o}	1.99	1.98	1.97	1.97	2.01	2.05	2.02

TABLE II:	Pressure Measu	rements vs. HU	1 Titration at 5	10 0

time, min	2	4	6	8	10	12	14	
reaction, % (press.)	13.2	20.4	33.6	42.4	49.7	55.8	61.3	
HCl, % (titration)	12.7	21.7	32.5	41.6	50.7	55.5	60.1	

TABLE III: Homogeneity of the Reaction at 370 °C

S/V	$10^4 k_1^{a}, s^{-1}$	$10^4 k_1, b \mathrm{s}^{-1}$	
1.0 6.0	$13.95 \\ 14.79$	12.01 11.80	

^a Clean Pyrex. ^b Allyl bromide seasoned.

tionally verified with a mass spectrometer and by infrared and nuclear magnetic resonance spectroscopy. The least-squares calculations were done with a Digital PDP 1145 computer.

The kinetics were performed in a static system⁴ with a Pyrex vessel of 232-mL capacity seasoned with allyl bromide^{6,7} and followed manometrically. The temperature was kept to better than ± 0.2 C with a calibrated platinum-platinum-13% rhodium thermocouple. No temperature gradient was found at different points along the reaction vessel. The chloride reagent was injected directly into the reaction vessel as described.⁸

Results and Discussion

In order to check the stoichiometry of reaction 1, in a

CH3 CH₃ $-\dot{c}$ -- CH_3 -- CH_3CO $--\dot{c}$ = CH_2 + HCi (1) CH3CO-

static system⁴ seasoned with allyl bromide, we carried out decompositions at different temperatures and up to 10 half-lives. In all cases, the final pressure, $P_{\rm f}$, was about twice the initial pressure, P_0 , as shown in Table I. Additional agreement was possible between the extent of decomposition as predicted from pressure measurements and from titration of hydrogen chloride produced (Table II).

To examine the effect of surface upon the rate of decomposition, we carried out several runs in a vessel with a surface-to-volume ratio of 6.0 relative to that of the normal vessel which is equal to one. When the packed and unpacked vessels are seasoned with allyl bromide, the reaction is homogeneous. However, in packed and un-

TABLE IV: Effect of Cyclohexene on Rates at 370 °C

•••••	$P_{\rm c}$, a torr	P_{i}^{b} torr	$P_{\rm c}/P_{\rm i}$	$10^4 k_1, \mathrm{s}^{-1}$
	62.5			11.95
	64.5	173	0.37	11.90
	78	154	0.51	11.46
	110	136	0.81	11.95
	63	61	1.03	11.95
	170	93	1.83	11.87

^a P_{c} = pressure of the chloride. ^b P_{i} = pressure of the inhibitor.

Scheme I

packed clean Pyrex vessels, a slight increase in the rates suggests a small heterogeneous effect (Table III). No induction period was apparent, and the addition of cyclohexane, and efficient free radical-chain inhibitor, resulted in no significant effect in the rate (Table IV). Therefore, this reaction is molecular in nature.

At a given temperature, the rate coefficient was invariable with changes in the initial pressure of the halide (Table V), and the first-order plots are satisfactorily linear to at least 70% decomposition. The variation of the rate coefficients with temperature is described in Table VI.

The data of Table VI were fitted to the following Arrhenius equation, where 80% confidence limits are being quoted: $\log k_1(s^{-1}) = (12.56 \pm 0.31) - (190.8 \pm 3.7) \text{ kJ mol}^{-1}$ $(2.303RT)^{-1}$.

Table VII shows the comparison between primary, secondary, and tertiary chlorobutanones with respect to their corresponding saturated hydrocarbon and compound of reference. The significantly higher rate of CH₃COC-H₂CH₂Cl relative to CH₃CH₂CH₂Cl and CH₃CH₂Cl arises, as recently reported,³ from the -M effect of the acetyl group. Because of this, the acidity of the β -hydrogen assists the leaving Cl atom in the elimination process of 4-chloro-2-butanone (Scheme I).

If one analyzes the effect of the CH₃CO group at the C_{α} -Cl bond in 3-chloro-2-butanone and 3-chloro-3methyl-2-butanone, an appreciable decrease in velocity of elimination is observed. This fact can be attributed to the electronic deactivation of the acetyl substituent with respect to CH_3 and CH_3CH_2 groups. Any consideration that steric factors may determine the rates of these halides must be disregarded. Charton's steric parameters¹⁶ of CH_3CO $(\nu = 0.50)$, CH₃CH₂ ($\nu = 0.56$), and CH₃ ($\nu = 0.52$) imply very close k values in the pyrolysis of these compounds. However, the actual experimental observation shows that the CH₃CO group has a significant retarding effect and that electronic factors are determinant in the rate of de-

⁽⁶⁾ Maccoll, A. J. Chem. Soc. 1955, 965.

⁽⁷⁾ Maccoll, A.; Thomas, P. J. J. Chem. Soc. 1955, 979.

⁽⁸⁾ Bridge, M. R.; Davies, D. H.; Maccoll, A.; Ross, R. A.; Banjoko, O. J. Chem. Soc. B 1968, 805.

⁽⁹⁾ Evans, P. J.; Ichimura, T.; Tschiukow-Roux, E. Int. J. Chem. Kinet. 1978, 10, 855.

⁽¹⁰⁾ Hartman, H.; Bosch, H. G.; Heydtmann, H. Z. Phys. Chem.
(Frankfurt am Main) 1964, 42, 329.
(11) Tsang, W. J. Chem. Phys. 1964, 41, 2487.

⁽¹²⁾ Heydtmann, H.; Rinck, G. Z. Phys. Chem. (Frankfurt am Main) 1961, 30, 250.

⁽¹³⁾ Maccoll, A.; Wong, S. W. J. Chem. Soc. B 1968, 1492.
(14) Chuchani, G.; Martin, I. J. Phys. Chem. 1980, 84, 3188.
(15) Benson, S. W.; O'Neal, H. E. Natl. Stand. Ref. Data Ser. (U.S.,

Natl. Bur. Stand.) 1970, 21.

⁽¹⁶⁾ Hansch, C.; Leo, A. J. "Substituent Constants for Correlation Analysis in Chemistry and Biology"; Wiley: New York, 1979.

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TABLE V:	Variation of	Rate Coefficient	ts with Initia	I Pressure at	370 °C				
P_{o}, t $10^{4}k$	$\mathbf{Orr} \\ \mathbf{s}_1, \mathbf{s}^{-1}$	62 7 11.90 1	8 1.46	110 11.95	122 11.88	165 11.83	170 11.87	191 11.95	
TABLE VI:	Variation of	Rate Coefficier	nts with Tem	perature					
tem 10 ⁴ k	p, °C z_1, s^{-1} Kinetic Par	340.0 3 1.97 3	49.0 .32 robutanones	360.0 6.65 at 400 °C	370.0 11.90	378.5 18.40	388.8 32.10	394.9 41.05	
	compd	$10^4 k_1, s^{-1}$	10 ⁴ k _H (1-olefin),	rel rate s ⁻¹ per H	E_{a}, kJ_{b}	mol	$\log A$, s ⁻¹	ref	
CH ₃ CH CH ₃ CH CH ₃ CC CH ₃ CC CH ₃ CC CH ₃ CC CH ₃ CC CH ₃ CC CH ₃ CC	1,Cl 1,CH,CH,Cl 2,CH,2CH,2Cl 4,Cl)CH,3 1,CH(Cl)CH,3 2,CCl(CH,3),2 1,CCl(CH,3),2 2,CCl(CH,3),2 1,CCl(CH,3),2 1,CCCL(CH,3),2 1,CCCL(CH	$\begin{array}{c} 0.12\\ 0.53\\ 1.56\\ 11.15\\ 35.01\\ 0.67\\ 1445.4\\ 3035.9\\ 56.53\end{array}$	$\begin{array}{c} 0.04\\ 0.27\\ 0.78\\ 3.72'\\ 5.01'\\ 0.22\\ 240.9d\\ 339.0'\\ 9.4\end{array}$	$1.0 \\ 6.8 \\ 19.5 \\ 1.0 \\ 2 \\ 1.3 \\ 0.06 \\ 1.0 \\ 1.4 \\ 0.04$	$\begin{array}{c} 241.8 \\ 230.7 \\ 225.2 \\ 213.8 \\ 208.3 \\ 205.8 \\ 188 \\ 184.1 \\ 190.8 \end{array}$	± 4.2 ± 3.1 ± 8.6 ± 4.1 ± 4.2 ± 2.6 ± 3.7	$\begin{array}{c} 13.84 \pm 0.20 \\ 13.63 \pm 0.23 \\ 13.67 \pm 0.69 \\ 13.64 \\ 13.71 \pm 0.36 \\ 11.80 \pm 0.33 \\ 13.77 \\ 13.77 \pm 0.25 \\ 12.56 \pm 0.31 \end{array}$	9 10 3 11 ^b 12 2 13 ^b 14 this work	

^a Rate coefficient toward one CH₃ substituent in CH₃CHClCH₃ pyrolysis. ^b Preferred value; see ref 15. ^c Value based on 43% yield of 1-butene at 400 °C. ^d Rate coefficient corresponds to the elimination of the two CH₃ groups, thus allowing a determination of the effect of the third CH₃ substituent. ^e Value based on 67% yield of 2-methyl-1-butene at 400 °C.

composition of organic chlorides in the gas phase. The present work further confirms that polarization of the C-Cl bond is the rate-determining event and the heterolytic nature of the transition state in the gas-phase pyrolysis

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of organic halides.⁴ Also, these results suggest the type of effect by which the acetyl substituent at the C_{α} -Cl and C_{β} -Cl bonds could influence the unimolecular gas-phase elimination of haloketones.

Spectroscopic Studies of Thin Film Polymer Laminates Using Raman Spectroscopy and Integrated Optics

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Calculation of the optical field intensity distribution within a multilayered asymmetric slab waveguide indicates that specific modes can be selected where a maximum optical field intensity exists either within one of the component layers or at the interface between two adjacent layers. Corresponding Raman measurements have been obtained from multilayered polymer waveguides composed of thin films ($\sim 1 \mu m$) of poly(vinyl alcohol) (PVA), polystyrene (PS), and poly(methyl methacrylate) (PMMA). The ability to observe Raman scattering from submicron films results because of the high optical field intensity which occurs within the films and the increased scattering volume afforded by integrated optical techniques. Results suggest that, in addition to studying the polymer/polymer interface, this technique provides a nondestructive method for investigating coatings using in this case the penetration of the evanescent tail of a wave guided in a PVA overlayer to obtain Raman scattering from the thin underlying film.

Introduction

Recently¹ there has been significant activity in the spectroscopic study of thin films primarily because, in addition to allowing investigation of exciting new molecular assemblies not present in bulk material, they also provide an indirect means of characterizing the surfaces on which they are deposited. Much interest has been generated in the Raman study of thin films and monolayers on metal surfaces²⁻⁷ because of the large enhancement factors

 $(10^{4}-10^{6})$ obtained. Understanding¹ this metallic enhancement mechanism has provided a considerable challenge within the scientific community, but its applicability as a general analytical technique is somewhat compromised because the experiments must be conducted either in an electrochemical cell or under high vacuum.

Spectroscopic investigations of thin polymer films have been reported⁸⁻¹⁵ but have generally been limited to the

⁽¹⁾ W. F. Murphy, Ed., "Proceedings of the VII International Conference on Raman Spectroscopy", Ottawa, 1980.

M. Fleishman, P. J. Hendra, and A. J. McQuillian, Chem. Phys. Lett., 26, 163 (1974).
 D. L. Jeanmarie and R. P. Van Duyne, J. Electroanal. Chem., 84,

⁽³⁾ D. L. Jeanmarie and R. P. Van Duyne, *J. Electroanal. Chem.*, 84, 1 (1977).

⁽⁴⁾ R. P. Van Duyne, J. Phys., Colloq. C5 (Suppl. 11), 38, 239 (1977).
(5) J. A. Creighton, M. G. Albrecht, R. E. Hester, and J. A. D. Mathew, them Phys. Lett. 55, 55 (1978).

Chem. Phys. Lett., 55, 55 (1978). (6) B. Pettinger, U. Wenning, and D. M. Kolb, Ber. Bunsenges. Phys. Chem., 82, 1326 (1978).

<sup>Chem., 82, 1326 (1978).
(7) J. C. Tsang and J. Kirtley, Solid State Commun., 30, 617 (1979).
(8) Y. Levy, C. Imbert, J. Cipriani, S. Racine, and R. Dupeyrat, Opt. Commun., 11, 66 (1974).</sup>