in cyclohexane and about a tenth of that in the absence of solvent. Thus, if anything, relatively more energy was transferred from the mercaptan molecules to the benzene molecules than the reverse. Furthermore, the values of $G_0{}^s$ for the isomerization (varying from 6×10^4 to 3.8×10^5) are obviously very much closer to the above-mentioned G values for mercaptan addition to the olefin than are the G_0 values (from about 1300 to 250, respectively).

An estimate of the chain length of the thiyl radical sensitized isomerization of polybutadiene can now be made. From a consideration of the results of Fontijn and Spinks cited above, it may be concluded that $G_0{}^s$ affords a reasonable measure of the number of *cis* double bonds isomerized per 100 e.v. absorbed directly and indirectly by the sensitizer. By analogy with the photolysis of diphenyl disulfide[6] using λ 2537, a quantum of around 5 e.v. in the radiation case can dissociate a molecule of $C_6H_5SSC_6H_5$ into $C_6H_5S\cdot$ radicals, so that about 40 such radicals can be produced per 100 e.v. absorbed by the disulfide. Because of cage effects and possible protection by benzene, it is likely that the number of radicals actually produced per 100 e.v. of energy absorbed by the disulfide will be much less than 40. At any rate, since a $G_0{}^s$ value as high as 4×10^5 was obtained in this work, it would follow that the $C_6H_5S\cdot$ radical can isomerize at least about 10^4 double bonds before being removed by any of the termination reactions discussed above. The chain length for the isomerization involving thiyl radicals is therefore of the same order of magnitude as that for the photochemical[7] and radiation chemical[5] addition of *n*-butyl mercaptan to pentene-1.

Acknowledgments.—The author wishes to thank R. J. Minchak and N. Hsu for kindly furnishing the high *cis*-polybutadiene used in this work, and Jane Ferguson and others of the infrared group for providing the required spectra.

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[6] W. E. Lyons, *Nature*, **162**, 1004 (1948).

[7] R. Back, G. Trick, C. McDonald and C. Sivertz, *Can. J. Chem.*, **32**, 1078 (1954).

BRECKSVILLE, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Photolysis of Polymethylvinyl Ketone and Polymethyl Isopropenyl Ketone[1]

BY K. F. WISSBRUN[2]

RECEIVED JULY 10, 1958

Films of polymethyl vinyl ketone and of polymethyl isopropenyl ketone have been photolyzed. Polymethyl vinyl ketone undergoes free radical dissociation and the Norrish Type II reaction. Polymethyl isopropenyl ketone degrades quantitatively to monomer, with a complicated dependence on molecular weight, temperature and intensity.

Introduction

The recent increased interest in the mechanisms of polymer degradation has resulted in a better understanding of the processes involved. Much of the work has been summarized in the books by Jellinek[3] and Grassie.[4] The techniques of photochemistry have proved useful in studying the mechanisms of polymer degradation. In the present work these techniques have been applied to the photolysis of polymethyl vinyl ketone (PMVK) and of polymethyl isopropenyl ketone (PMIK). These polymers are suitable for such study because the photochemistry of ketones is comparatively well understood. Also, the role of the carbonyl group as an intermediate in the photoöxidation of polymers makes a better knowledge of its behavior in polymeric systems desirable.

During the course of this work the results of Guillet and Norrish[5] on the photolysis of dioxane solutions of PMVK were published. The present work, done on films of the polymer rather than on solutions, agrees with that of Guillet and Norrish.

Experimental

Materials.—Anhydrous methyl vinyl ketone, distilled at 190 mm. under nitrogen, was degassed in a vacuum line, and a 70-g. sample was distilled into a bulb containing 0.585 g. of recrystallized benzoyl peroxide. The distillate was frozen at −196°, the bulb was sealed and allowed to stand 16 hr. at room temperature. The resulting clear, colorless gel was dissolved in chloroform and precipitated with excess benzene six times. The yield of dried polymer was about 2 g.; the intrinsic viscosity in acetone at 25° was 1.13 dl./g., corresponding to a molecular weight of about 200,000 from the data of ref. 5.

Thin films of PMVK were prepared by casting from a filtered dilute chloroform solution on mercury. The films, plasticized by residual solvent, were too soft and adherent to be handled easily, and they were therefore cast in a rectangular glass frame. After evaporation of the bulk of the solvent the frame was placed in a heated vacuum desiccator until the film was sufficiently dry to cut into 12 mm. square samples for the photolyses. Two series, designated B and C, were photolyzed. In each series the film thickness, determined by weighing and by optical density, was uniform to better than 5%. Assuming a density of 1.12 for the polymer,[6] the thicknesses were calculated to be 15.9 and 47.3 μ, respectively.

Three samples of PMIK were used in this work. The first, designated as G, was kindly supplied by the Celanese Corporation of America and was stated to have been prepared in 70% conversion in cyclohexane solution with azobisisobutyronitrile catalyst. The polymer was purified by repeated precipitation from chloroform solution by methanol, and a film was then cast on mercury.

The other two samples, designated K and L, were prepared by a method similar to that used for PMVK. Polymer

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[1] This research was supported in part by contract AF 18(600)1528 with the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command. Reproduction in whole or in part is permitted for any purpose by the United States Government. The author wishes to express appreciation to Dr. W. A. Noyes, Jr., for discussions about this work.

[2] Research Laboratory, Celanese Corporation of America, Summit, New Jersey. Postdoctoral Fellow 1955–1957 under a grant to the Department of Chemistry, University of Rochester, by the Doctors Camille and Henry Dreyfus Foundation, Inc.

[3] H. H. G. Jellinek, "Degradation of Vinyl Polymers," Academic Press, Inc., New York, N. Y., 1955.

[4] N. Grassie, "Chemistry of High Polymer Degradation Processes," Interscience Publishers, Inc., New York, N. Y., 1956.

[5] J. E. Guillet and R. G. W. Norrish, *Proc. Roy. Soc.* (*London*), **A233**, 153 (1955).

[6] T. White and R. N. Haward, *J. Chem. Soc.*, 25 (1943).

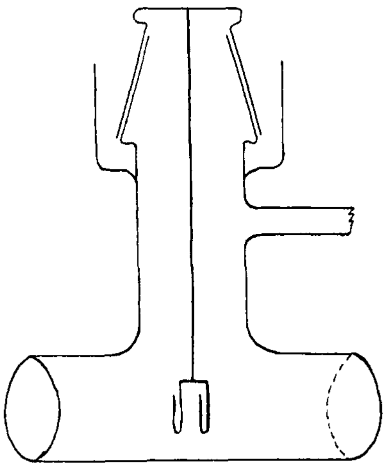

Fig. 1.—Cell with film holder.

K was polymerized at 28° with 0.72% benzoyl peroxide, L at 52° with 0.11% catalyst. These samples were purified by repeated precipitation from acetone by water, followed by precipitation from chloroform solution by methanol. The intrinsic viscosities at 25° in methyl ethyl ketone of G, K and L were 0.43, 0.65 and 0.33 dl./g., respectively. The films of G were 14.5 μ thick; the optical densities at 2900 Å. for G, K and L were 0.89, 1.06 and 0.88, respectively.

Apparatus.—For photolysis a film was placed on a glass "fork" (Fig. 1) which was fused to a ground outer joint cap. The cap and the corresponding mercury-sealed inner joint were marked so that the holder could be placed into the cell reproducibly. The cell was jacketed by an insulated aluminum furnace, whose temperature was controlled manually by a Variac and measured by a chromel–alumel thermocouple. The furnace temperature usually remained constant during a run to within 1°, and the temperature variation within the cell was probably less than this.

For the PMVK work the optical system consisted of a Hanovia S-100 medium pressure mercury arc, a stop, a quartz lens and the Hunt-Davis[7] filter combination (2.5 cm. of 0.10 g./l. potassium chromate, 2.5 cm. of 300 g./l. nickel chloride hexahydrate and 1 cm. of 5 g./l. potassium biphthalate) in front of the cell; at the back window was a 3 mm. sheet of Corning 9863 glass and a RCA 935 phototube. The transmitted light was measured by the deflection of a galvanometer on a scale 2 m. from the mirror. In order to obtain higher intensities for the PMIK work, this system was modified by filtering the incident light only by 2 mm. of Pyrex; the transmitted light was focussed through the above filter combination upon the phototube. In each case diethyl ketone at 150° was used as an actinometer. The main absorbed wave length in both cases was 3130 Å.

The cell was connected to a conventional vacuum line so arranged that products condensable at −196° did not come into contact with stopcock grease. For mass-spectrometric analysis condensables were frozen into break-seal tubes; non-condensable gases were transferred to analysis tubes by a Toepler pump behind a mercury float-valve cut-off. Samples for ultraviolet absorption analysis were frozen into a ring-sealed trap behind another such cut-off. For the PMIK work a RCA 1946 thermocouple gauge was attached to the cell line.

The photolysis of PMIK was shown by mass spectra to produce almost pure monomer. The rate of monomer evolution was followed by measuring the pressure on the thermocouple gauge. The gauge was calibrated by producing monomer photolytically, freezing it into a trap and dissolving in distilled water for analysis by ultraviolet absorption. The extinction coefficient of methyl isopropenyl ketone was measured independently and was found to be 8.48 ± 0.12 l. mole^{-1}cm.$^{-1}$ in water at 2200 Å. This value agreed well with that calculated from the weight loss on photolysis of PMIK, assuming that the loss was due only to monomer.

The intrinsic viscosity measurements were done with a semi-micro dilution viscometer similar to the one described by Hart.[8]

Results and Discussion

PMVK.—The effect of irradiation upon the molecular weight of PMVK was determined as a function of film thickness, temperature and incident intensity. These data are shown in Table I; the relative decrease of intrinsic viscosity with irradiation is plotted in Fig. 2.

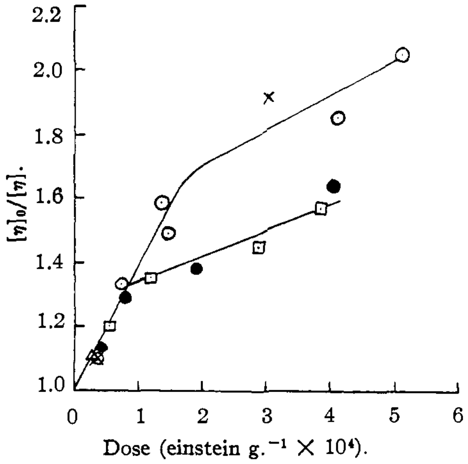

Fig. 2.—Photolysis of PMVK—relative decrease of intrinsic viscosity *vs.* absorbed radiation

○ $I_a \sim 5.3 \times 10^{-11}$ einstein sec.$^{-1}$
× $I_a \sim 0.7 \times 10^{-11}$
△ $I_a \sim 0.07 \times 10^{-11}$
} Film thickness 16μ, $T = 28°$

● $T = 28°$
⊡ $T = 80°$
} Film thickness 47μ, $I_a \sim 5 \times 10^{-11}$ einstein sec.$^{-1}$

It is apparent from Fig. 2 that there is an initially linear region which is independent of film thickness, of intensity and of temperature. The independence of temperature and of intensity is continued in the non-linear portions of the plot.

TABLE I

PHOTOLYSIS OF POLYMETHYL VINYL KETONE

Irradiation time (sec. × 10^{-3})	Absorbed intensity (einstein sec.$^{-1}$ × 10^{11})	Total quanta (einstein × 10^7)	Quanta per gram (einstein g.$^{-1}$ × 10^4)	Temp. (°C.)	$\frac{[\eta]_0}{[\eta]}$
Series B (film thickness 16 μ)					
7.20	4.8	3.5	1.36	28	1.59
7.20	5.2	3.7	1.49	28	1.49
3.60	5.7	2.1	0.74	28	1.33
25.2	5.1	12.9	5.12	28	2.05
18.0	5.8	10.5	4.10	28	1.85
1.80	5.4	0.97	0.37	28	1.10
10.8	0.74	0.80	0.32	28	1.10
103.5	.64	6.6	3.02	28	1.92
101.0	.071	0.72	0.27	28	1.11
Series C (film thickness 47 μ)					
12.9	4.7	6.1	0.81	28	1.29
33.2	4.1	13.6	1.92	28	1.38
60.9	5.0	30.5	4.04	28	1.64
5.60	5.2	2.9	0.40	28	1.13
44.5	5.4	24.0	3.53	28	1.59
9.36	4.5	4.2	0.52	80	1.20
23.2	4.2	9.7	1.20	80	1.35
47.1	4.5	21.2	2.86	80	1.45
71.1	4.8	34.1	3.84	80	1.57

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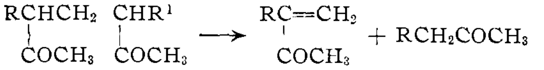
[7] R. E. Hunt and W. Davis, Jr., THIS JOURNAL, **69**, 1415 (1947).

[8] V. E. Hart, *J. Polymer Sci.*, **17**, 207 (1955).

In this region the curves no longer coincide for films of different thickness because of the non-uniform light intensity through the films.

Qualitatively these results agree with those of Guillet and Norrish,[5] who irradiated PMVK in dioxane solution. They attributed the observed decrease of molecular weight to the Type II re-



$$\underset{\displaystyle COCH_3}{RCHCH_2}\ \underset{\displaystyle COCH_3}{CHR^1} \longrightarrow \underset{\displaystyle COCH_3}{RC{=}CH_2} + RCH_2COCH_3$$

action in part because of the temperature independence of the chain scission process. The occurrence of the Type II reaction predicts the formation of double bonds conjugated with carbonyl groups, which should cause absorption in the neighborhood of 2300 Å. This prediction was confirmed by Guillet and Norrish and in this work, as shown in Fig. 3.

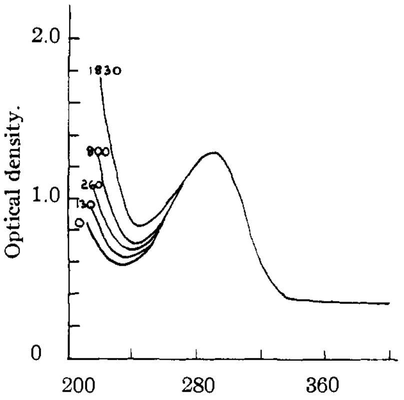


Fig. 3.—Photolysis of PMIK–change of ultraviolet spectrum with time of irradiation (min.).

Assuming that the viscosity decrease is solely due to the Type II reaction, one may estimate the quantum yield as follows. The relative decrease of the number average degree of polymerization is given by

$$\frac{P_0}{P} - 1 = \frac{aP_0}{m}$$

where P is the degree of polymerization, P_0 its initial value, a the total moles of bonds broken, and m the monomoles of sample. Then

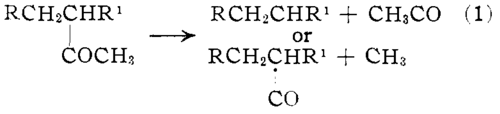
$$a = \Phi I_a t$$

where Φ is the quantum yield of the chain scission reaction and $I_a t$ the total number (einstein) of quanta absorbed. Hence

$$\frac{P_0}{P} - 1 = M_0 \Phi \frac{I_a t}{g}$$

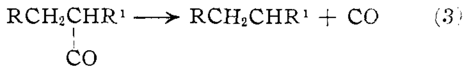
where M_0 is the initial molecular weight and g the sample weight. From the slope of the initial portion of Fig. 2 Φ is then calculated to be 0.02. (Here it has been estimated from the intrinsic viscosity that M_0 is 200,000, and it has been assumed that the molecular weight is proportional to the intrinsic viscosity. If instead one assumes that the exponent in the Staudinger relation is 0.7, the calculated value of Φ becomes 0.03). The agreement with the value 0.025 estimated by Guillet and Norrish is gratifying. That the quantum yield of chain scission is independent of the medium, as well as of temperature and intensity, is further evidence that the reaction is intramolecular, since this has been shown to be characteristic of the Type II reaction in other systems.[9-11]

The small samples used in these experiments made determination of the volatile photolysis products difficult. However, a film was photolyzed 16 hr. at 80° and the products analyzed mass-spectrometrically. The products found were acetaldehyde, carbon monoxide and methane, with quantum yields of 0.06, 0.003 and 0.0006, respectively. Instrument background made the values, particularly of the latter two, somewhat uncertain. At the same temperature Guillet and Norrish found quantum yields of about 0.01 for all three. They account for the formation of these products by the free radical reactions



$$\underset{\displaystyle COCH_3}{RCH_2CHR^1} \longrightarrow \begin{array}{c} RCH_2CHR^1 + CH_3CO \\ \text{or} \\ \underset{\displaystyle CO}{RCH_2CHR^1} + CH_3 \end{array} \qquad (1)$$

$$CH_3CO \longrightarrow CH_3 + CO \qquad (2)$$



$$\underset{\displaystyle CO}{RCH_2CHR^1} \longrightarrow RCH_2CHR^1 + CO \qquad (3)$$

$$CH_3 + RH \longrightarrow CH_4 + R \qquad (4)$$

$$CH_3CO + RH \longrightarrow CH_3CHO + R \qquad (5)$$

Instead of (5) which was found not to occur in the photolysis of liquid acetone,[12] we prefer to let acetaldehyde be formed by disproportionation in a cage of the two radicals formed in (1). This could account for the higher quantum yield of acetaldehyde in bulk photolysis and for the correspondingly lower methane and carbon monoxide yields.

PMIK.—Upon photolysis PMIK evolved large amounts of what was shown by mass-spectrometric analysis to be essentially pure monomer. After an induction period the rate of monomer production became constant, at least to about 5% conversion. After irradiation was stopped monomer continued to be evolved for a short time. A similar phenomenon has been observed in the photolysis of polymethyl methacrylate,[13] where it was explained as a consequence of the slowness of diffusion of monomer through the viscous polymer. It was found that the induction period decreased from about nine minutes at 150° to three minutes at 190°, which is consistent with Cowley and Melville's explanation.

The variation of the rate of monomer production with intensity was determined by placing neutral density filters before the front cell window. In earlier experiments copper screens were used to

(9) (a) R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1934); (b) R. G. W. Norrish, *Trans. Faraday Soc.*, **33**, 1521 (1937); (c) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1521, 1531 (1938).

(10) W. Davis, Jr., and W. A. Noyes, Jr., THIS JOURNAL, **69**, 2153 (1947).

(11) P. Ausloos, *Canadian J. Chem.*, **36**, 383 (1958).

(12) P. E. Frankenburg and W. A. Noyes, Jr., THIS JOURNAL, **75**, 2847 (1953).

(13) P. R. E. J. Cowley and H. W. Melville, *Proc. Roy. Soc. (London)*, **A210**, 461 (1952); **A211**, 320 (1952).

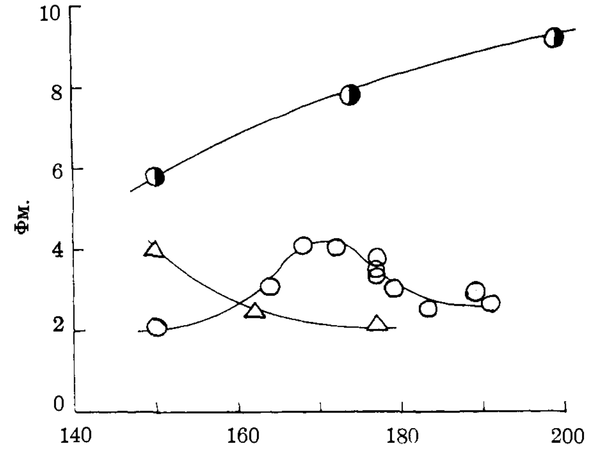


Fig. 4.—Photolysis of PMIK–quantum yield of methyl isopropenyl ketone as a function of temperature: ○, polymer G; ◑, polymer K; △, polymer L.

reduce the light intensity; it was found, however, that these served only to reduce the area illuminated, rather than the intensity of incident light. In Table II are shown the results of these experiments at 150 and 177° for polymer G. By plotting log rate against log intensity a straight line is obtained whose slope is the intensity exponent; the values found were 0.41 at 150° and 0.73 at 177°.

Table II

Variation of Methyl Isopropenyl Ketone Quantum Yield with Intensity

Temp. (°C.)	Absorbed intensity (einstein sec.$^{-1}$ $\times 10^{11}$)	Rate (mole sec.$^{-1}$ $\times 10^{11}$)	Φ_M (mole einstein^{-1})
150	22.6	32.9	1.46
150	21.8	35.8	1.64
150	1.9	12.9	6.8
150	1.3	10.2	7.8
150	12.4	25.6	2.06
177	10.8	38.0	3.5
177	11.8	45.3	3.8
177	4.0	19.7	4.9
177	3.7	16.0	4.3
177	3.8	16.9	4.4
177	8.6	29.0	3.4
177	2.2	16.0	7.3
177	2.1	10.0	4.8

The dependence of the monomer quantum yield upon temperature at constant intensity was studied; the results are shown in Fig. 4. In Fig. 5 is shown the intrinsic viscosity of polymer G as a function of conversion to monomer. The small initial sample weight limited these experiments to about 20% conversion.

Along with the large amount of monomer small quantities of methane and carbon monoxide were produced by photolysis. Instrument background made it difficult to do more than determine maximum values to these. It was found that the minimum ratio of monomer to carbon monoxide was about 300 and the minimum ratio of monomer to methane about 1000.

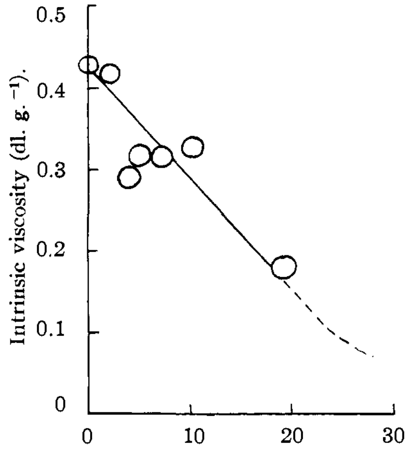
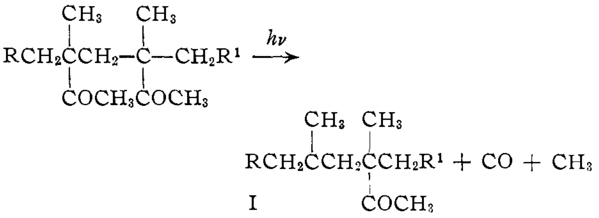


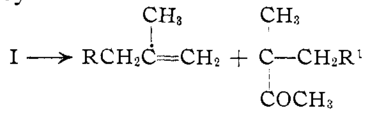
Fig. 5.—Photolysis of PMIK–intrinsic viscosity of residual polymer *vs.* % conversion to monomer.

It is evident that the mechanism of the photodegradation of PMIK is too complex to be deduced from these data and that only a very general discussion of the steps involved is possible. The rapid drop of molecular weight as monomer is evolved is accounted for by a random initiation step



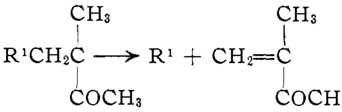
$$\mathrm{RCH_2\underset{COCH_3}{\overset{CH_3}{C}}CH_2{-}\underset{COCH_3}{\overset{CH_3}{C}}{-}CH_2R^1} \xrightarrow{h\nu} \underset{\mathrm{I}}{\mathrm{RCH_2\overset{CH_3}{C}CH_2\underset{COCH_3}{\overset{CH_3}{C}}CH_2R^1}} + \mathrm{CO} + \mathrm{CH_3}$$

followed by



$$\mathrm{I} \longrightarrow \mathrm{RCH_2\overset{CH_3}{C}{=}CH_2} + \mathrm{\underset{COCH_3}{\overset{CH_3}{C}}{-}CH_2R^1}$$

Monomer may then be formed by the usual unzipping reaction



$$\mathrm{R^1CH_2\underset{COCH_3}{\overset{CH_3}{C}}} \longrightarrow \mathrm{R^1} + \mathrm{CH_2{=}\underset{COCH_3}{\overset{CH_3}{C}}}$$

At low temperatures the intensity exponent is about 0.5, indicating that termination is second order. As the temperature is increased, the monomer quantum yield goes through a maximum and the intensity exponent rises. Furthermore, the temperature at which the maximum occurs appears to increase with increasing molecular weight. Apparently another termination step, a first-order process, competes with radical–radical termination at high temperature.

A tentative explanation of these findings may be offered. It must be assumed that the unzipping polymeric radical can participate in a chain transfer reaction, presumably by abstraction from another polymer molecule. Then, if the kinetic chain length of unzipping increases with temperature, at some temperature depending upon the molecular weight of the polymer, complete unzipping of the polymer chains will occur. The small radical resulting from unzipping may be unable to take part in the chain transfer reaction, either because it is evaporated, as has been suggested in the case of polymethyl methacrylate,[18] or because it is resonance-stabilized by an unsaturated chain end. In either case the effect is to decrease the number of unzipping chains produced by each initiation step, thereby reducing the quantum yield of monomer, and to introduce a first-order chain termination step, thereby increasing the intensity exponent. The verification of such a mechanism would be very difficult, particularly when one considers such complications as the effect of melt viscosity, which depends on temperature and molecular weight, and on diffusion-controlled termination reactions.

SUMMIT, NEW JERSEY

[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE]

Nuclear Magnetic Resonance Study of the Protolysis and Ionization of N-Methylacetamide[1]

BY A. BERGER, A. LOEWENSTEIN AND S. MEIBOOM

RECEIVED JUNE 23, 1958

The rate and mechanism of protolysis in N-methylacetamide (I) in aqueous solution has been investigated by the nuclear magnetic resonance technique. The protolysis was found to be both acid and base catalyzed, the reaction rate being proportional to the amide concentration and to the hydrogen ion or hydroxyl ion concentration. It was found that in N,N-dimethylacetamide (II) free rotation around the C–N bond occurs on acidification. This phenomenon is closely related to the protolysis in I, both being due to protonation at the nitrogen atom. It could be shown, however, from a study of the n.m.r. spectrum in very acidic solution, that the protonation occurs predominantly at the oxygen, both ionic species being in equilibrium. A detailed mechanism for the exchange reactions is proposed.

Introduction

In this paper we report measurements of the protolysis kinetics in N-methylacetamide by the nuclear magnetic resonance (n.m.r.) technique.[2] This compound is of special interest, as it provides the simplest model of the RCONHR′ grouping characteristic of peptides. Its chemical and physical properties have been studied extensively.[3–7]

Exchange rates of the amide hydrogens in proteins[8] and polypeptides[9] have been measured by isotope labelling and the results obtained were interpreted in terms of the extent and stability of the hydrogen bonds formed by the amide groups. However, in the absence of stable hydrogen bonds, *e.g.*, in low molecular weight peptides, the exchange is too fast to be measured by isotope labelling. Direct measurements of the reaction constants in the absence of hydrogen bonding, as well as an understanding of the reaction mechanism can be obtained from n.m.r. spectra. This technique is a powerful tool in the study of fast exchange reactions, being applicable to reactions with half-life times between about 1 and 0.001 of a second.

The n.m.r. spectrum of N-methylacetamide in aqueous solution at *p*H 5 is shown in Fig. 1. From left to right (in order of increasing frequency) this spectrum shows a single line due to the C-methyl hydrogens, a doublet due to the N-methyl hydrogens, the water line and a broad line due to the amide hydrogen. The splitting of the N-methyl resonance is a result of spin–spin interaction with the amide hydrogen. The sharpness of the components of this doublet shows that the rate of exchange of the amide hydrogen is relatively slow, the half-life time being more than one second.

The resonance of the amide hydrogen would be expected to show a triplet structure because of spin–spin interaction with the N^{14} nucleus (spin 1), with a superposed quadruplet structure from interaction with the N-methyl group. However, because of the fast quadrupole relaxation of the N^{14} nucleus only one broadened line is actually observed.[10]

Figure 2 shows the changes in the N-methylacetamide n.m.r. spectrum when the *p*H of the solution is varied. The observed changes are the result of the increased rate of exchange of the amide hydrogen. Note the broadening of the water line, which is the result of hydrogen exchange between the water and the NH group.

An additional and unexpected feature of the spectrum, which is not resolved in Figs. 1 and 2, should be mentioned. It was found that a spin–spin interaction of about 0.45 c./s. exists between the C-methyl and the N-methyl hydrogens. These interactions are observed at the highest resolution obtainable and with very slow passage. In acidic and basic solutions, where the amide hydrogen exchanges rapidly, and its spin–spin interactions are averaged out, both methyl resonances are quadruplets (see Fig. 3). At a *p*H of about 5, where the ex-

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[1] This research has been sponsored in part by the Air Force Office of Scientific Research of the Air Research and Development Command, USAF, through its European Office, under Contract No. AF 61 (052)-03.

[2] While this work was in progress, M. Takeda privately communicated to us that he had measured the protolysis of N-methylacetamide in acid solution by the n.m.r. technique.

[3] S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954, pp. 117–152; "Advances in Protein Chem.," **9**, 299 (1954).

[4] L. R. Dawson, P. G. Sears and R. H. Graves, THIS JOURNAL, **77**, 1986 (1955).

[5] A. R. Goldfarb, A. Mele and N. Gutstein, *ibid.*, **77**, 6194 (1955).

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