

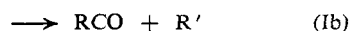
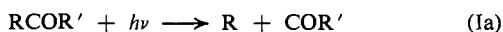
Relations between Photodecomposition Modes and Molecular Structure in the Series of Carbonyl Compounds, $n\text{-C}_3\text{H}_7\text{COR}^1$

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Abstract: The vapor-phase photolysis of a series of carbonyl compounds of general structure $n\text{-C}_3\text{H}_7\text{COR}$ was studied at 3130 Å as a function of temperature and pressure. The R group was varied in the series H, CH₃, C₂H₅, $n\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$, $i\text{-C}_4\text{H}_9$, $sec\text{-C}_4\text{H}_9$, $t\text{-C}_4\text{H}_9$, in order to evaluate the effect of structure upon the individual primary photodissociative processes and the relationship between these processes. Quantum yields of carbon monoxide and ethylene products were used as measures of the type-I ($n\text{-C}_3\text{H}_7\text{COR} + h\nu \rightarrow n\text{-C}_3\text{H}_7\text{CO} + \text{R}$ and $n\text{-C}_3\text{H}_7 + \text{COR}$) and type-II [$n\text{-C}_3\text{H}_7\text{COR} + h\nu \rightarrow \text{C}_2\text{H}_4 + \text{CH}_2=\text{C}(\text{OH})\text{R}$] primary photodissociative modes in the ketones. A number of correlations were noted between the structural features and the efficiency of the type-II rearrangement. One striking effect was the relation between ϕ_{II} and the extent of alkyl substitution on the α -carbon atom of the R group. An empirical rule was formulated which relates molecular structure and the ϕ_{II} values for the n -propyl ketones.

The photochemistry of the aliphatic ketones has been the subject of extensive investigation for many years, and considerable progress has been realized in the elucidation of the various photophysical and photochemical changes which these compounds undergo.³ All of the aliphatic ketones photodissociate to some degree by free-radical processes Ia and Ib.



The more complex ketones which have γ -hydrogen atoms in the alkyl groups attached to the carbonyl carbon atom also react to a significant extent by an intramolecular rearrangement to yield an olefin molecule and a ketone of smaller size.



Existing data allow certain generalizations to be made concerning the detailed mechanism of the type-II process. Evidence suggests that the process proceeds through the intermediate formation of the enol form of the final ketone product.⁴ Presumably the H-atom transfer involves a six-membered-ring intermediate.⁵ Process II may occur in a concerted single step, or, alternatively, in a stepwise process which leads ultimately to the enol ketone and olefin. It appears that both singlet and triplet states of the ketone can react by the type-I and -II processes,⁶ although the extent of participation of each remains uncertain in most cases.

(1) Submitted by C. H. N. in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, 1965.

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(3) For a general review of the area and references to the original literature see (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 377; (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 154, 224.

(4) (a) R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 5061 (1959); (b) G. R. McMillan, J. G. Calvert, and J. N. Pitts, Jr., *ibid.*, **86**, 3602 (1964).

(5) (a) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938); (b) W. Davis, Jr., and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **69**, 2153 (1947).

(6) (a) V. Brunet and W. A. Noyes, Jr., *Bull. Soc. Chim. France*, 121 (1958); (b) R. P. Borkowski and P. Ausloos, *J. Phys. Chem.*, **65**, 2257 (1961); (c) P. Ausloos and R. E. Rebbert, *J. Am. Chem. Soc.*, **83**, 4897 (1961); (d) R. P. Borkowski and P. Ausloos, *ibid.*, **84**, 4044 (1962); (e) J. L. Michael and W. A. Noyes, Jr., *ibid.*, **85**, 1027 (1963); (f) P. Ausloos and R. E. Rebbert, *ibid.*, **86**, 4512 (1964); (g) R. E. Rebbert and P. Ausloos, *ibid.*, **86**, 4803 (1964); (h) P. J. Wagner and G. S. Hammond,

In addition to the two primary processes I and II in ketone photolyses, a third process occurs leading to the isomerization of the ketone to cyclobutanol derivatives.^{6c,7} This interesting process has been studied only in a limited fashion for a very few systems.

Some structural effects on the primary efficiency of the type-I and -II processes have been noted. Thus the efficiency of the type-II process has been correlated qualitatively with the number of γ -hydrogen atoms in the ketone,⁸ the type of H atom abstracted (primary, secondary, tertiary),⁹ the electrical and steric influence of substituents on the abstracting power of the ketone, and the nature of the excited states [³(n, π^*), ¹(n, π^*), ³(π , π^*), etc.].¹⁰ However, it is impossible to attempt meaningful quantitative comparisons between ketone quantum yield data and molecular structure from the existing published data, since there is no uniformity in the experimental conditions employed; the use of different light sources, filter systems, actinometry, temperature, pressure, methods of analysis, and other experimental variables can introduce indeterminable variations in the apparent quantum efficiency values found. In this work we have attempted to study carefully a complete series of structurally related ketones using standardized techniques and carefully controlled experimental conditions. We report in this paper a study of the vapor-phase photolyses at 3130 Å of the carbonyl compounds of structure $n\text{-C}_3\text{H}_7\text{COR}$, where R is H, CH₃, C₂H₅, $n\text{-C}_3\text{H}_7$, $i\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$, $sec\text{-C}_4\text{H}_9$, $i\text{-C}_4\text{H}_9$, $t\text{-C}_4\text{H}_9$. From these self-consistent data, one might hope to formulate correlations between structure and the efficiency of the type-I and -II primary processes.

Experimental Section

The Photochemical System. The photolysis system was similar to that used in these laboratories and described previously.¹¹ The

ibid., **87**, 4009 (1965); **88**, 1245 (1966); (i) R. B. Cundall and A. S. Davies, *Trans. Faraday Soc.*, **62**, 2444 (1966).

(7) N. C. Yang and D. D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

(8) J. W. Kraus and J. G. Calvert, *ibid.*, **79**, 5921 (1957).

(9) P. Ausloos, *J. Phys. Chem.*, **65**, 1616 (1961).

(10) (a) J. N. Pitts, Jr., L. D. Hess, E. J. Baum, E. A. Schuck, J. K. S. Wan, P. A. Leermakers, and G. F. Vesley, "Progress in Photobiology," E. J. Bowen, Ed., Blackwell, Oxford, 1965; (b) E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **88**, 2652 (1966).

only significant change was the use of three ultra-high vacuum metal valves in the photolysis system housed in the air thermostat. The light source was a Hanovia S-500 medium-pressure mercury arc mounted and operated as described previously.¹² The light was filtered to isolate the 3126–3132-Å region of the spectrum.¹³ The beam of filtered radiation was rendered nearly parallel and limited to fill the cell volume practically completely through the use of two quartz lenses and two light stops. The emerging beam was focused onto the cathode of an RCA-935 phototube by a third quartz lens, and the output of the tube was continually monitored with a recorder.

The Analytical System. The equipment employed for product analysis consisted of a temperature-programmed, gas-solid chromatograph and a mass spectrometer used in conjunction with a Blacet-Leighton gas buret. At the completion of a photochemical run the product gases not condensable at liquid nitrogen temperature (largely CO and CH₄) were removed with a Toepler pump and analyzed by mass spectrometry. The very small amount of ethylene in this fraction was added to the major quantity which was determined chromatographically in the condensable fraction. The condensable fractions were chromatographed using a 5-ft column of 1% squalene on 20–60 mesh activated alumina. Nonlinear temperature programming was employed from ambient temperature to 185°.

Materials. Standard samples were all research grade materials: CO (Matheson Co.), hydrocarbons (Phillips Petroleum Co. or Matheson Coleman and Bell). The reactant ketones were obtained from several sources and purified as described: acetone (Baker and Adamson, reagent grade) was dried over MgSO₄ (anhydrous), fractionated on an all-glass column (75 plates), and checked for purity by column chromatography; diethyl ketone (Eastman Kodak, White Label), methyl *n*-propyl ketone (Bios Laboratories, best source found for a 3-pentanone-free product), di-*n*-propyl ketone, methyl *n*-butyl ketone, methyl *sec*-butyl ketone (K & K Laboratories), ethyl *n*-propyl ketone, isopropyl *n*-propyl ketone, and the four isomeric butyl propyl ketones were custom synthesized by Edcan Laboratories. All of the ketones and *n*-butyraldehyde (Matheson Coleman and Bell) were purified by chromatography using an Aerograph Autoprep A-700 equipped with a 20-ft Carbowax 20M column. The column temperature was selected at 5–10° above the boiling point of the ketone. The detector was run at a temperature 10° higher than that of the column and the collector and injector assemblies were operated 25–50° above the maximum column temperature. Careful control of the chromatography conditions and collection of small center cuts gave samples which appeared to be of 99.95% minimum purity, and these were used in the photochemical experiments. Styrene was an Eastman Kodak White Label product purified by multiple bulb-to-bulb distillations at reduced pressure.

Actinometry. Diethyl ketone was employed as an internal chemical actinometer throughout this work. The quantum yield of carbon monoxide formation was taken as unity¹⁴ at 3130 Å and 130°. The results obtained with this system checked well with intensity measurements made using acetone at 100°¹⁵ and K₃Fe(C₂O₄)₃ actinometry¹⁶ in several experiments. Actinometric photolyses were performed before and after a series of experiments with each of the compounds. A slow linear decay of the incident intensity occurred throughout the entire study. The actinometer data together with the daily photometer readings made possible accurate interpolation to determine the incident intensity for any specific photolysis within a series.

Results

Molar Extinction Coefficients. The following data were determined by averaging four to seven individual measurements at different pressures at the temperatures shown; the reproducibility of the measurements was ±0.10 l./mole cm. The values of ϵ [$\epsilon = (\log I_0/I)/cl$ l./mole cm] are: *n*-butyraldehyde, 10.90 (100°), 10.76

(11) R. M. Smith and J. G. Calvert, *J. Am. Chem. Soc.*, **78**, 2345 (1956).

(12) Reference 3a, p 695.

(13) Reference 3a, p 732.

(14) L. M. Dorfman and Z. D. Sheldon, *J. Chem. Phys.*, **17**, 511 (1949).

(15) D. S. Herr and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **62**, 2052 (1940).

(16) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956).

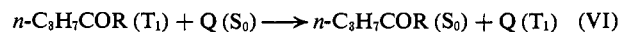
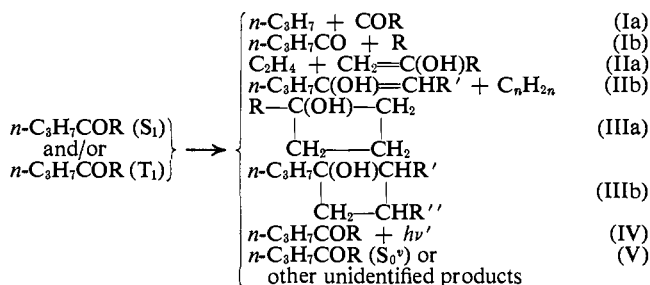
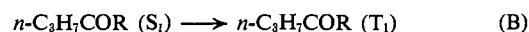
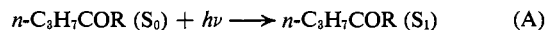
(60°); methyl *n*-propyl ketone, 5.75 (150°), 5.17 (100°), 4.54 (60°); ethyl *n*-propyl ketone, 6.77 (150°), 5.79 (100°), 4.96 (60°); di-*n*-propyl ketone, 8.03 (150°), 7.03 (100°), 6.62 (60°); isopropyl *n*-propyl ketone, 9.78 (150°), 8.94 (100°), 8.28 (60°); *n*-butyl *n*-propyl ketone, 8.03 (150°), 7.51 (110°), 6.84 (75°); isobutyl *n*-propyl ketone, 9.51 (150°), 8.56 (110°), 8.14 (75°); *sec*-butyl *n*-propyl ketone, 12.57 (150°), 12.25 (110°), 12.12 (75°); *t*-butyl *n*-propyl ketone, 11.77 (150°), 11.03 (110°), 10.55 (75°).

Quantum-Yield Data. The experimental conditions and the quantum yields of the products of the carbonyl compounds *n*-C₃H₇COR are summarized in Table I. In order to avoid appreciable photodecomposition of reaction products, the possible buildup of quencher products, and other complications, the percentage conversion was limited to 0.5% or less in all experiments except for two runs with *sec*-butyl *n*-propyl ketone (see footnote *b* of Table I). These were extended to approximately 1.5% decomposition to facilitate analysis for the product ketones.

In two runs using *t*-butyl *n*-propyl ketone (Table I, footnotes *c* and *d*) styrene was added. Styrene is essentially transparent to 3130-Å radiation, but subsequent reactions with free radicals led to significant polymerization of the styrene as evidenced by a relatively rapid rate of loss in transmitted light intensity.

Discussion

The Estimation of Primary Quantum Efficiencies in the Photolysis of the Propyl Ketones. The established photochemistry of the simple aliphatic ketones readily suggests a general primary reaction mechanism which may be considered for the *n*-propyl ketones studied in this work.



Presumably the primary processes Ia and Ib would be followed by H-atom abstraction, disproportionation, combination, and decomposition reactions of the various radicals formed initially. One may anticipate from published rate constant data¹⁷ that the acyl radical decomposition reactions (RCO → R + CO) will be the dominant mode of reaction of these radicals at the relatively low intensities and high temperatures employed in this study; radical-radical interactions leading in part to dicarbonyl compound formation should be unimportant. Thus the quantum yield of carbon monoxide formation should be a reliable estimate of $\phi_{1a} + \phi_{1b}$ for these conditions.

(17) J. A. Kerr and J. G. Calvert, *J. Phys. Chem.*, **69**, 1022 (1965).

Table I. Data from the Vapor-Phase Photolyses of the Carbonyl Compounds, $n\text{-C}_3\text{H}_7\text{COR}$, at 3130 Å

Compound	Pressure, mm	Temp, °C	I_a , quanta/ cell sec $\times 10^{-13}$	Quantum yields of products															
				CO	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	<i>n</i> -C ₄ - H ₁₀	<i>n</i> -C ₅ - H ₁₂	<i>n</i> -C ₆ - H ₁₄	2-Methyl- pentane						
<i>n</i> -C ₃ H ₇ CHO	21.4	99.6	8.26	1.19		0.176													
	19.6	59.2	8.17	0.67		0.164													
<i>n</i> -C ₃ H ₇ COCH ₃	49.4	149.2	7.96	0.43	0.31	0.246			0.049	0.25	0.020								
	29.8	151.1	5.06	0.43	0.32	0.250			0.052	0.22	0.023								
	65.5	99.3	9.82	0.36	0.21	0.266			0.020	0.15	0.033								
	46.4	99.4	7.35	0.33	0.20	0.249			0.021	0.13	0.038								
	29.7	99.4	4.96	0.35	0.16	0.250			0.022	0.12	0.046								
	47.1	58.4	7.16	0.15	0.04	0.253			0.019	0.06	0.045								
<i>n</i> -C ₃ H ₇ COC ₂ H ₅	58.0	150.6	14.0	0.57		0.191 ^a	0.39	0.025	0.36	0.019	0.024	0.013							
	40.5	150.4	9.75	0.58		0.207 ^a	0.35	0.026	0.37	0.021	0.029	0.015							
	57.7	99.5	9.34	0.57		0.217 ^a	0.28	0.024	0.31	0.044	0.060	0.032							
	40.9	99.7	6.62	0.61		0.206 ^a	0.27	0.029	0.30	0.048	0.069	0.034							
	25.5	99.7	3.80	0.71		0.222 ^a	0.25	0.033	0.27	0.060	0.085	0.046							
	62.9	62.7	11.0	0.46		0.216 ^a	0.17	0.028	0.19	0.062	0.094	0.042							
$(n\text{-C}_3\text{H}_7)_2\text{CO}$	43.3	61.9	7.89	0.48		0.219 ^a	0.15	0.030	0.17	0.071	0.112	0.048							
	34.1	150.8	5.57	0.37		0.210			0.035	0.54		0.023							
	65.8	151.0	8.62	0.37		0.217			0.031	0.56		0.016							
	33.8	100.3	4.74	0.40		0.210			0.028	0.39		0.058							
	32.3	61.3	4.46	0.26		0.209			0.029	0.23		0.083							
<i>n</i> -C ₃ H ₇ COCH- (CH ₃) ₂	27.1	149.7	14.2	(0.79)		0.157			0.094	0.65		0.025	0.080						
	17.1	149.9	9.52	0.63		0.154			0.105	0.58		0.030	0.096						
	38.5	100.0	18.7	0.70		0.112			0.139	0.56		0.055	0.167						
	26.8	100.0	13.9	0.68		0.111			0.143	0.51		0.064	0.184						
	17.0	100.1	9.35	0.66		0.113			0.144	0.44		0.071	0.193						
	26.9	63.3	14.0	0.78		0.088			0.180	0.37		0.110	0.257						
15.9	59.4	8.92	0.76		0.082			0.189	0.33		0.123	0.275							

Compound	Pressure, mm	Temp, °C	I_a , quanta/ cell sec $\times 10^{-13}$	Quantum yields of products															
				CO	C ₂ H ₄	C ₃ H ₆	C ₃ H ₈	1- C ₄ H ₈	2- C ₄ H ₈	<i>i</i> - C ₄ H ₈	<i>n</i> - C ₄ H ₁₀	<i>i</i> - C ₄ H ₁₀	<i>n</i> - C ₆ H ₁₄	C ₇ H ₁₆					
<i>n</i> -C ₄ H ₉ COCH ₂ CH ₂ CH ₃	33.5	150.6	15.1	0.10	0.036	0.247	0.07	0.011			0.066	0.0							
	21.2	150.2	10.6	0.10	0.034	0.250	0.07	0.010			0.061	0.0							
	33.1	109.7	15.5	0.07	0.029	0.242	0.05	0.0			0.048	0.0							
	20.3	109.7	10.1	0.07	0.029	0.245	0.05	0.0			0.046	0.008							
	20.8	76.4	10.3	0.05	0.024	0.237	0.03	0.0			0.032	0.009							
<i>i</i> -C ₄ H ₉ COCH ₂ CH ₂ CH ₃	28.5	150.0	14.7	0.24	0.055	0.149	0.15			0.034	0.14	0.013							
	17.5	150.0	9.45	0.24	0.055	0.152	0.13			0.033	0.13	0.013							
	18.2	109.1	9.88	0.18	0.053	0.162	0.087			0.013	0.10	0.017							
	56.8	109.1	23.7	0.22	0.053	0.152	0.11			0.012	0.12	0.013							
<i>sec</i> -C ₄ H ₉ COCH ₂ CH ₂ CH ₃ ^b	17.3	75.2	9.33	0.16	0.060	0.174	0.053			0.012	0.074	0.023							
	21.6	149.5	11.6	0.36	0.123	0.019	0.23	0.012	0.045		0.14	0.017	0.032 ^e						
	19.5	109.4	11.0	0.38	0.103	0.027	0.19	0.013	0.060		0.12	0.039	0.067 ^e						
<i>t</i> -C ₄ H ₉ COCH ₂ CH ₂ CH ₃	20.7	76.7	13.0	0.44	0.078	0.028	0.12	0.011	0.058		0.085	0.051	0.080 ^e						
	25.3	149.4	16.2	0.52	0.116	0.042	0.23	0.170				0.15	0.044	0.061 ^f					
	14.9	149.6	10.3	0.56	0.120	0.048	0.21	0.182				0.15	0.053	0.069 ^f					
	43.7	109.1	24.9	0.58	0.089	0.054	0.22	0.196				0.17	0.069	0.086 ^f					
	14.4	109.1	10.2	0.55	0.097	0.060	0.19	0.205				0.17	0.089	0.098 ^f					
	14.3	76.1	10.4	0.63	0.073	0.064	0.16	0.209				0.17	0.103	0.110 ^f					
	14.1 ^c	108.9	9.27	0.54	0.092	0.0	0.035	0.014				0.0	0.0	0.0					
13.9 ^d	109.7	8.54	0.51	0.092	0.0	0.013	0.020				0.0	0.0	0.0						

^a These data were corrected for the contribution from the mutual disproportionation of ethyl radicals and the cross-disproportionation of ethyl and *n*-propyl radicals to obtain the summary data of Tables II and III; the disproportionation to combination ratios employed for the correction were 0.11 for the ethyl-ethyl reaction [D. P. Dingley and J. G. Calvert, *J. Am. Chem. Soc.*, **85**, 856 (1963)] and 0.045 for the *n*-propyl-ethyl reaction (J. O. Terry and J. H. Futrell, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965). ^b In runs at 60.5 mm, 149°, $I_a = 22.0 \times 10^{13}$, and at 65.7 mm, 109°, $I_a = 20.9 \times 10^{13}$, the quantum yields of methyl *sec*-butyl ketone were 0.062 and 0.053, respectively, and those of ethyl *n*-propyl ketone were 0.061 and 0.050, respectively. ^c Also 4.8 mm of styrene was added in this run. ^d Also 20.1 mm of styrene was added in this run. ^e This product was 3-methylhexane. ^f This product was 2,2-dimethylpentane.

The ethylene and propylene products are derived primarily from processes IIa and IIb. It can be shown from the published rate constant data¹⁸ that the alkyl radical decomposition reactions (e.g., $n\text{-C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$) must be unimportant sources of these products for our conditions. However, one must consider the possible olefin formation from radical disproportiona-

tion reactions. In the case of ethyl *n*-propyl ketone photolysis, the disproportionation reactions ($\text{C}_2\text{H}_5 + n\text{-C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_4 + \text{C}_3\text{H}_8$; $2\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$), in addition to process II, could lead to a significant rate of formation of ethylene. This rate can be determined through the known ratios of rates of the disproportionation to the combination reactions for the ethyl and propyl systems and the measured rates of the combination products, *n*-butane, *n*-pentane, and *n*-hexane (see

(18) W. E. Morganroth and J. G. Calvert, *J. Am. Chem. Soc.*, **88**, 5387 (1966).

Table I). The corrections to derive ϕ_{IIa} from $\Phi_{C_3H_7}$ values were small in all cases (1.7–5.8%). In the estimation of ϕ_{IIb} in the photolyses of the *n*-butyl and isobutyl *n*-propyl ketones, similar corrections for propylene formed in disproportionation reactions were anticipated but were found to be negligible for our conditions of relatively low light intensity.

Thus from each ketone studied a reliable estimate of $\phi_{Ia} + \phi_{Ib}$, ϕ_{IIa} , and ϕ_{IIb} can be made from the product quantum-yield data. A summary of these estimates, derived as described, is given in Table II for the temperature of 150° common to all the studies.

Table II. Summary of Quantum Yields for Primary Processes I and II in the Photolyses of the *n*-Propyl Ketones ($n-C_3H_7COR$) at 3130 Å and 150°^a

R	$\phi_{Ia} + \phi_{Ib}$		ϕ_{IIa}	ϕ_{IIb}	$\Sigma\phi_i$
	ϕ_{IIa}	ϕ_{IIb}			
H	0.35 ^b	0.17 ⁰	...	0.17	0.52
CH ₃	0.42 ⁶	0.25 ²	...	0.25	0.68
C ₂ H ₅	0.57 ²	0.20 ³	...	0.20	0.78
<i>n</i> -C ₃ H ₇	0.37 ²	0.10 ^{6c}	0.10 ^{6c}	0.21	0.58
<i>i</i> -C ₃ H ₇	0.70 ⁸	0.15 ^{5d}	...	0.16	0.86
<i>n</i> -C ₄ H ₉	0.10 ³	0.03 ⁵	0.24 ⁸	0.28	0.39
<i>i</i> -C ₄ H ₉	0.23 ⁷	0.05 ⁵	0.15 ¹	0.21	0.44
<i>sec</i> -C ₄ H ₉	0.35 ⁸	0.06 ^{2d}	0.06 ^{1d}	0.12	0.48
<i>t</i> -C ₄ H ₉	0.53 ⁶	0.11 ^{8d}	...	0.12	0.65

^a The values reported represent the arithmetic average of individual values at 150° except for those ketones for which the type-II process is independent of temperature; the tabular values for ϕ_{IIa} and ϕ_{IIb} represent the arithmetic average of all individual values at all temperatures in these cases. ^b Estimate from *n*-C₃H₇CHO photolysis with added I₂ reported in ref 19. ^c Values are obtained by dividing the total olefin yield by 2, assuming equal participation by the two equivalent sides of the molecule. ^d The type-II yields are definitely temperature dependent.

The data determined here are in excellent agreement with the limited published data for the three compounds of the series which have been studied quantitatively previously. For the conditions similar to those employed in this study (3130 Å, gas phase, 60–150°), the following data have been reported: for *n*-C₃H₇CHO,¹⁹ $\phi_{II} = 0.16$ (0.17 found here); for methyl *n*-propyl ketone, $\phi_{II} = 0.29$,²⁰ 0.27,²¹ 0.24^{6c} (0.25 found here); for di-*n*-propyl ketone, $\phi_{II} = 0.22$ ²² (0.21 found here). It is probable that the absolute quantum-yield data of Table I are accurate to $\pm 5\%$, and the relative quantum yields are probably good to $\pm 2\%$.

Relations between Structure and the Quantum Efficiency of the Primary Processes. (a) General Observations. The summary of quantum-yield data of Table II reveals several interesting relations between molecular structure of the ketone and the quantum yields of the primary processes. Observe in Table II, column 2, that $\phi_{Ia} + \phi_{Ib}$ values show a rather random variation in magnitude over a considerable range (0.10

for R = *n*-C₄H₉ to 0.71 for R = *i*-C₃H₇). One might have naively expected Φ_{CO} to be highest in the *t*-butyl *n*-propyl ketone case since this compound has the weakest carbon-carbon bond adjacent to the carbonyl group. However the Φ_{CO} for the ethyl *n*-propyl ketone is even higher than that of the *t*-butyl *n*-propyl ketone. Obviously factors in addition to the product radical stability influence ϕ_I values.

From a qualitative point of view, the fraction of *n*-C₃H₇COR compounds which undergo the type-II process is surprisingly constant with variation in R. Note the data of column 5 of Table II. One might have anticipated that the type-I and type-II processes would be in competition and that large variations in ϕ_{II} would occur as the rate constants for the excited molecule reactions, which result in the primary processes I and II, were altered by variation in the R group. However, this is not the case.

In Table II there is no simple correlation evident between the number of γ -H atoms present in the compound and the ϕ_{II} values. For example, although the di-*n*-propyl ketone and the isobutyl *n*-propyl ketone contain twice and three times, respectively, the number of γ -H atoms as the methyl and ethyl *n*-propyl ketones, the total type-II process quantum yields are nearly the same for all four compounds. However, when there are different competitive type-II processes possible within the same excited molecule, and the different processes both involve the transfer of a primary H-atom, there is a reasonably good statistical distribution of the products observed. Thus in the *sec*-butyl *n*-propyl ketone one expects equal yields of processes IIa and IIb from purely statistical reasoning; in this case abstraction of any one of three primary H-atoms by the carbonyl oxygen is involved in both reactions IIa and IIb. This is the observed result. In the photolysis of the isobutyl *n*-propyl ketone one expects statistically twice the quantum yield of the propylene as the ethylene product since abstraction of any one of six γ -H atoms leads to propylene, while abstraction of any one of three γ -H atoms may lead to ethylene formation. Actually the propylene to ethylene ratio is 2.7; apparently some structural preferences beyond that of statistics favors the propylene-forming reaction somewhat. In each of these cases involving the abstraction of primary H atoms in the γ position there is no significant activation energy difference between the processes, and the quantum yields are temperature independent.

When H atoms of different type are present in the γ position, a significant preference is shown for abstraction of the one of weaker C-H bond dissociation energy, and the quantum efficiencies of the competitive processes are temperature dependent. However, the sum of the two yields, $\phi_{IIa} + \phi_{IIb}$, is substantially independent of temperature. Note the data for *n*-butyl *n*-propyl ketone in Tables I and II. Here the propylene product is greatly favored over the ethylene in spite of the adverse 2:3 ratio of the number of secondary to primary H atoms in the γ position. An Arrhenius plot of the ratio $\Phi_{C_3H_4}/\Phi_{C_2H_6}$ gives an apparent activation energy difference between the reaction involving primary H-atom abstraction and that involving the secondary H atom of 1.3 kcal/mole. This result is in good agreement with the similar difference of 0.9 kcal/mole derived from the data of Ausloos⁹ from the 3130-Å pho-

(19) F. E. Blacet and J. G. Calvert, *J. Am. Chem. Soc.*, **73**, 667 (1951).

(20) R. P. Borkowski and P. Ausloos, *J. Phys. Chem.*, **65**, 2257 (1961).

(21) J. N. Pitts, Jr., A. D. Osborne, and R. Martin, unpublished results.

(22) C. R. Masson, *J. Am. Chem. Soc.*, **74**, 4731 (1952).

tolysis of 4-methyl-2-hexanone. In that case 1-butene and 2-butene are formed as a primary H atom and a secondary H atom, respectively, are abstracted from the different γ -carbon positions in the same R group of the ketone. The discrimination between different types of H atoms observed here is also in accord with the preference found for H-atom over D-atom abstraction in the type-II process in 2-pentanone-4,5,5-*d*₃ photolysis studied by Borkowski and Ausloos.^{6b}

An examination of the data of Table II shows that the $\phi_{IIa} + \phi_{IIb}$ values are independent of the temperature within the experimental error for the compounds n -C₃H₇COR with R = H, CH₃, C₂H₅, n -C₃H₇, n -C₄H₉, and i -C₄H₉. However, for the three ketones studied which contain multiple α -alkyl substituents (R = i -C₃H₇, sec -C₄H₉, t -C₄H₉), the very unusual result of a temperature dependence to the ϕ_{II} values is seen. This corresponds to an apparent activation energy of ethylene formation of about 2 kcal/mole in each case. In each of these three ketones there appears to be a smaller inverse temperature dependence to ϕ_I (-0.7 kcal/mole) such that $\phi_I + \phi_{II}$ is approximately independent of the temperature.

There is an interesting quantitative relation between the extent of the α -alkyl substitution in the propyl ketones and the size of ϕ_{II} which can be seen from an examination of the data. For example, the data from runs at 150° show a regular decrease in the ϕ_{II} values for the n -C₃H₇COR ketones in the order R = CH₃ ($\phi_{II} = 0.252$), C₂H₅ ($\phi_{II} = 0.203$), i -C₃H₇ ($\phi_{II} = 0.155$), t -C₄H₉ ($\phi_{II} = 0.118$). Substitution of one methyl group for a methyl hydrogen atom in the methyl n -propyl ketone lowers the quantum yield of type-II process by a factor of 0.80; a second methyl substitution in the α position lowers ϕ_{II} by a factor of 0.76; and a third methyl substitution in the α position lowers ϕ_{II} again by an identical factor, 0.76. The consistency of the magnitude of the lowering of the ϕ_{II} values with α substitution suggests that the effect is real although its detailed mechanistic explanation is open to question. A similar effect is seen if one compares the ϕ_{II} values for di- n -propyl ketone and sec -butyl n -propyl ketone. Introduction of an α -methyl group in the di- n -propyl ketone lowers $\phi_{IIa} + \phi_{IIb}$ by a factor of 0.6. From the near-constancy of the $\phi_{IIa} + \phi_{IIb}$ values for the series of n -C₃H₇COR ketones with R = C₂H₅, n -C₃H₇, i -C₄H₉ (0.20, 0.21, 0.21), it appears that the nature of the α -alkyl substituent is not highly important in determining ϕ_{II} as long as only primary H atoms are present in the γ positions.

A rather surprising inefficiency of molecular decomposition can be seen from a study of the quantum yield data for the propyl ketones. Limited qualitative work in our laboratory confirms the occurrence of primary process III in the propyl ketones²³ and is consistent with the Ausloos and Rebbert data for methyl n -propyl ketone which show $\phi_{III} \cong 0.04$ at 150° and 15 mm pressure. Weak emission has been observed in the 3130-Å photolysis of n -butyraldehyde and methyl n -propyl ketone²⁴ at 30°. However, the dissociative

lifetimes of the aliphatic ketones decrease significantly with increase in temperature and with increasing molecular complexity,^{6f} so it is probable that $\phi_{IV} < 0.01$ at 150° for all of the ketones studied here. If the reasonable assumption that $\phi_{III} + \phi_{IV} \leq 0.05$ for our conditions of photolysis of the n -propyl ketones is coupled with the data for the summation of the quantum efficiencies for the various photodissociative modes (column 6 of Table II), it is apparent that the ultimate fate of a large fraction of the excited molecules is not accounted for by processes I through IV. Process V, the internal conversion of electronic energy, is one obvious manner to rationalize these data. Either a return to the original ground-state ketone is a very important mode of reaction of the excited molecules ($T_1 \rightarrow S_0$, and/or $S_1 \rightarrow S_0$) or there is an unidentified major product of the photolyses, perhaps a transient species, which ultimately re-forms the ketone.²⁵

It may be significant that only those alkyl ketones containing a side chain of three or more carbon atoms in length have the sum of the photodissociative processes less than unity at temperatures above 100°. Acetone, methyl ethyl ketone, diethyl ketone, and diisopropyl ketone all have $\phi_{IIa} + \phi_{IIb} = 1.0$ for temperatures above 100° and at normal pressures and light intensities. The apparent inefficiency in the photodissociation of the larger ketones may be rationalized by possible mechanisms to be considered in the following section.

(b) **Considerations of the Nature of the States and the Mechanisms Involved in the Primary Processes in the 3130-Å Photolyses of the n -C₃H₇COR Ketones.** In an attempt to add new information on the nature of the electronic states involved in the n -C₃H₇COR ketone photolyses at 3130 Å, styrene was added as a triplet quencher in the photolysis of t -butyl n -propyl ketone (see Table I and footnotes *c* and *d*). The experimental conditions of these runs were essentially the same as those of the fourth run of this compound except for the styrene addition. Although styrene has been shown to be the most efficient acetone triplet quencher of a great variety of olefins studied by Ausloos and Rebbert,²⁶ there was no detectable influence of styrene addition on either the ethylene or the carbon monoxide quantum yields. However, an almost quantitative removal of free-radical products of n -C₃H₇ and t -C₄H₉ resulted. Since Φ_{CO} was unaffected by the styrene addition, the free-radical product suppression must have occurred through the radical addition to the styrene; this is consistent also with the induced polymerization of the styrene observed in this system.

Obviously the only warranted conclusion from our styrene-ketone studies is that the electronic state or states responsible for the type-I and type-II processes in t -butyl n -propyl ketone photolysis are extremely short-lived. If one makes the generous estimate that a 10% reduction in Φ_{CO} or $\Phi_{C_2H_4}$ is the smallest change

(24) P. Ausloos and E. Murad, *J. Phys. Chem.*, **65**, 1519 (1961).

(25) This suggestion is stimulated by the work of W. A. Noyes, Jr., W. A. Mulac, and M. S. Matheson, *J. Chem. Phys.*, **36**, 880 (1962), and recent data from biacetyl photolysis by J. Lemaire, University of Texas, to be published. It appears that a transient species formed by α - or β -hydrogen-atom transfer to the carbonyl may be an important intermediate which leads to the apparent internal conversion process in biacetyl and possibly in other ketones.

(26) P. Ausloos and R. E. Rebbert, *J. Am. Chem. Soc.*, **87**, 5569 (1965).

that could be detected in these runs with added styrene and further assumes that k_{VI} is near the collision number, then the lifetimes of the excited state or states from which the type-I and -II processes originate in *t*-butyl *n*-propyl ketone are less than about 10^{-9} sec. If a triplet state is involved in the photodecomposition reactions in this system, then the rate constant for intersystem crossing, k_B , is surprisingly large.

For only one of the propyl ketones studied here are there any published data which delineate the nature of the excited states involved in the type-II process; these were determined in methyl *n*-propyl ketone photolysis at 3130 Å by Michael and Noyes,^{6e} Ausloos and Rebbert,^{6f} and Wagner and Hammond.^{6h} Perhaps the most significant of all of the findings is that the singlet emission of the methyl *n*-propyl ketone is unaffected by biacetyl addition at pressures where considerable quenching of ethylene results.^{6f} This suggests strongly that the energy transfer to biacetyl occurs by way of the excited triplet state of the ketone, and that this state is the precursor to the type-II process at 3130 Å in methyl *n*-propyl ketone photolysis.

The data of Michael and Noyes^{6e} on the quenching of the ethylene quantum yield with biacetyl addition and the sensitized emission from the biacetyl can be treated to derive an estimate of k_{II} . If one assumes that the rate constant for the energy-transfer step, k_{VI} , is equal to the collision number, 7.7×10^{11} l./mole sec, the Michael and Noyes ethylene quenching data give $k_{II} \cong 3.0 \times 10^8 \text{ sec}^{-1}$ at 32.5° and $5.3 \times 10^8 \text{ sec}^{-1}$ at 56°. The sensitized emission data yield independent estimates of $k_{II} \cong 2.7 \times 10^8 \text{ sec}^{-1}$ at 32.5° and $3.6 \times 10^8 \text{ sec}^{-1}$ at 56°. The two results are quite self-consistent and check well with the similar solution phase data of Wagner and Hammond ($k_{II} \cong 1.2 \times 10^8 \text{ sec}^{-1}$ at room temperature). The temperature dependence of the data of Michael and Noyes suggests that the activation energy E_{II} of the process II in methyl *n*-propyl ketone photolysis at 3130 Å is about 4.8 kcal/mole.²⁷ This value for E_{II} is entirely consistent with the estimate of $E_{II} \cong 5.5$ kcal/mole which one can derive independently from the k_{II} estimate of Michael and Noyes at one temperature and a reasonable estimate²⁸ for the preexponential factor for the type-II reaction, $A_{II} \cong 2.7 \times 10^{12} \text{ sec}^{-1}$.

In the case of the 3130-Å photolysis of methyl *n*-butyl ketone, both the data of Michael and Noyes and that of Wagner and Hammond suggest that the excited singlet state is the origin of a larger fraction of the type-II process than with methyl *n*-propyl ketone. In the solution-phase work it was estimated that 40% of the type-II process originates from the excited singlet; this fraction may be significantly greater in the gas-phase experiments of Michael and Noyes.^{6e} Wagner and

Hammond reasoned that the presence of secondary H atoms in the γ position in this compound may increase the rate constant for the type-II process for the S_1 state such that the rate of this reaction becomes comparable to that of the rate of intersystem crossing. However, in studies of liquid 2-octanone, which also contains secondary H atoms equivalent to those in methyl *n*-butyl ketone, Dougherty²⁹ found that 80–82% of the type-II process occurred by way of the triplet state. Apparently factors in addition to the ease of H-atom abstraction are also operative in determining the nature of the excited state precursor to the type-II process. In particular the polarity of the solvent seems to influence markedly the extent of the type-II process in solution.³⁰

From all of the evidence at hand, one must conclude that the excited states from which process II originates are extremely short-lived. Furthermore it seems probable that the major reactant for the type-II process is the triplet state in the 3130-Å photolysis of most of the propyl ketones studied in this work. In the one compound in this study in which secondary H atoms are available in the γ position, *n*-butyl *n*-propyl ketone, a significant contribution of singlet to the type-II products appears to be likely.

The state or states which are the origin of the primary processes Ia and Ib in the 3130-Å photolysis of the *n*-C₃H₇COR ketones is less clear. Cundall and Davies⁶ⁱ and Ausloos³¹ favor the dominant participation of the triplet state in process I as well as II in methyl *n*-propyl ketone photolysis. The most compelling evidence is that of Ausloos³¹, who found that, in the excited benzene (triplet) or mercury (³P₁) sensitized photolyses of methyl *n*-propyl ketone at 2537 Å, ϕ_I is larger than that found in the direct photolysis at 3130 Å.

Some of the present data are qualitatively consistent with the origin of processes Ia, Ib, IIa, and IIb in competitive reactions of the same electronic state, presumably the triplet. Thus one might suggest that the α -substituent effect observed correlates with the decreasing strength of the *n*-C₃H₇CO-R bond and leads to the increasing importance of process I over II as the more highly branched R radicals are substituted. It is probably reasonable that the value of k_{II} would be essentially invariant for the series of compounds *n*-C₃H₇COR with R = CH₃, C₂H₅, *i*-C₃H₇, and *t*-C₄H₉, where equal types and numbers of γ -H atoms are present in the ketones. Thus to explain the variation of ϕ_{II} and the temperature dependence of process II as α -alkyl substitution is increased, one must assume that $E_{II} = E_I$ for the compounds in which R in *n*-C₃H₇COR is a primary radical (H, CH₃, C₂H₅, *n*-C₃H₇, *n*-C₄H₉, or *i*-C₄H₉), but E_I must become progressively less than E_{II} for the series where R = C₂H₅, *i*-C₃H₇, *t*-C₄H₉.

However, there are some inconsistencies of the present data with an assumed origin of the primary processes I and II from the same state. If the process II occurred as one of several competitive reactions involving the same excited state, one would expect $\phi_{IIa} + \phi_{IIb}$ from di-*n*-propyl and isobutyl *n*-propyl ketones to be considerably greater than that observed in the ethyl *n*-propyl case, since twice and three times as many H

(29) T. J. Dougherty, *J. Am. Chem. Soc.*, **87**, 4011 (1965).

(30) T. J. Dougherty, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract V-36.

(31) Private communication to the authors.

(27) Only the ethylene yield data of Michael and Noyes can be used in estimating E_{II} (as they suggest), since the temperature dependence of the biacetyl emission is complicated by the increased rate of triplet biacetyl decomposition at the higher temperature.

(28) This estimate is derived from the average of the adjusted preexponential factors (in sec^{-1}) for the analogous thermal reactions of olefin elimination which probably involve an analogous transition state: acetic anhydride (0.7×10^{12}), ethyl acetate (3.2×10^{12}), isopropyl acetate (5.0×10^{12}), and *t*-butyl acetate (2.1×10^{12}); constants are from the summary table of A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press Inc., New York, N. Y., 1955, p 129, where references to the original literature are given. The values for acetic anhydride and isopropyl and *t*-butyl acetates were corrected to the same number (3) of γ -H atoms by taking one-half, one-half, and one-third, respectively, of the experimental A factors.

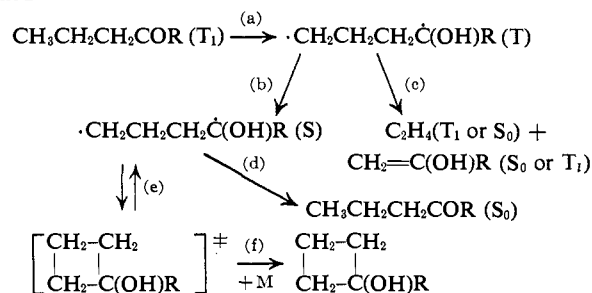
atoms of the identical type are present in the di-*n*-propyl and isobutyl *n*-propyl ketones, respectively, and the $n\text{-C}_3\text{H}_7\text{CO-R}$ bond-dissociation energy is not greatly different for these ketones. However, the ϕ_{II} values are almost the same in the three cases: 0.20, 0.21, and 0.21, respectively. Although it is possible that this result is completely fortuitous, it seems more likely to us that the result is meaningful; it supports the suggestion that the processes I and II occur from different excited states. The reasoning which points to this conclusion should be considered. The excited singlet ketone may be converted to some precursor state (possibly T_1) with an efficiency which is relatively invariant to the structural changes seen in these three ketones, and, in spite of the appreciable energy barrier of about 5 kcal/mole and the different A factors for process II in these ketones, a fixed fraction of the state must always react by process II. It seems unlikely to us that process I could be in competition with II and maintain the observed results, since it is highly improbable that the activation energy and preexponential factors for steps Ia and Ib would be of such varied magnitude as to maintain the constant sum of $\phi_{\text{IIa}} + \phi_{\text{IIb}}$ for these ketones. It seems more likely to us that process I occurs from some other state, conceivably a dissociative state formed from the first excited singlet.

The strong indication cited above that there is an appreciable activation energy for the excited-state reaction to form the type-II products is consistent with the fact that there is an observable activation energy difference of 1.3 kcal/mole between the type-II reactions involving the abstraction of secondary and primary H atoms in the γ position. However, one must rationalize these results with the apparently conflicting observation that ϕ_{II} is much less than unity and is independent of temperature for the $n\text{-C}_3\text{H}_7\text{COR}$ compounds with $R = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7,$ and $i\text{-C}_4\text{H}_9$. The observed temperature independence of ϕ_{II} alone would be compatible with a common singlet or triplet state as the reactant for primary processes I and II provided that the activation energies for the competing modes of reaction of the excited state are near to that for process II. However, the near-constancy of the ϕ_{II} values with the variation of the structure and the number of γ -H atoms in these ketones discussed previously makes this mechanism unattractive. If the triplet state is the major source of the type-II process at 3130 Å, as seems likely, then one must invoke a peculiar pattern of reactions to maintain the insensitivity of ϕ_{II} to temperature and the structure of the ketone. We must assume that the extent of the alternative reactions of the excited singlet state formed on excitation is determined by probabilities of intersystem crossing to the triplet state, the dissociative excited states involving the $\text{R-COR}'$ bonds, etc., which are insensitive to variations in temperature and minor changes in the structure of the alkyl group R in the $n\text{-C}_3\text{H}_7\text{COR}$ ketones. ϕ_{II} will then be temperature independent for either of the following conditions: (1) the triplet state reacts exclusively by process II; or (2) the rate constants for the competitive reactions of the triplet state have an identical temperature dependence. Since the primary process III, as well as II, in methyl *n*-propyl ketone is quenched by biacetyl addition,^{6f} a common state for primary pro-

cesses II and III is probable, and the second alternative seems most likely.

Obviously the requirement that processes II and III have identical activation energies will be met if the rate-determining step in both processes is the same reaction of γ -H-atom abstraction by the excited carbonyl oxygen. However, as Ausloos and Rebert pointed out, II and III cannot involve simply two competitive reactions of the same precursor, since ϕ_{II} is unaffected by changes in temperature, pressure, etc., while ϕ_{III} is very sensitive to the experimental conditions. For example, in methyl *n*-propyl ketone photolysis at 3130 Å, $\phi_{\text{III}} = 0.04$ (150°, 15 mm), 0.11 (28°, 32 mm), 0.08 (28°, 15 mm), 0.03 (28°, 3 mm); on the other hand, for the entire range of pressure and temperature ϕ_{II} showed no significant variation. Of the mechanisms considered by Ausloos and Rebert, one involving the favored occurrence of III from the lower vibrational modes of the excited state seemed most attractive. However, the nonoccurrence of III at high temperatures or low pressures could not be compensated by other observed modes of decomposition. They felt this unaccounted for fraction of precursor to process III may return to the ground-state ketone by some undefined path, or, conceivably, participate in process I. A possible alternative scheme seems to fit well the facts at hand (Scheme I). According to this re-

Scheme I



action sequence the triplet excited state reacts by path a to form the triplet diradical species which is destroyed only by alternative paths b and c. Presumably the triplet diradical cannot form the cyclobutanol product by ring closure without spin inversion. Its reaction by path b forms the singlet diradical while reaction by path c forms the type-II products. Possibly either the olefin or the enol product of path c is formed in its lowest triplet state so that net spin is conserved. By this mechanism the singlet diradical either undergoes ring closure to form a vibrationally excited cyclobutanol derivative (path e), or the H atom on the carbonyl is transferred back to the γ -carbon atom to re-form the ground-state ketone with the net internal conversion of energy, path d. According to this scheme the cyclobutanol product is favored over internal conversion when vibrational relaxation is effected by collisional processes in reaction f; thus the highest ϕ_{III} values would be found at the highest gas pressures and in solution-phase photolyses as is observed. The mechanism affords an isolation of the two precursors to the primary processes II and III, yet provides for their common origin in a fashion which seems to fit the known information well.

If one accepts the hypothesis that the two processes I and II occur from different electronic states, then the observed α -alkyl substituent effect noted for the ketones

$n\text{-C}_3\text{H}_7\text{COR}$ in the sequence $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7,$ and $t\text{-C}_4\text{H}_9,$ must be rationalized in a different manner from that which has been given above. Several interesting alternatives exist.

(1) Conceivably the α -alkyl substituent effects result from an enhanced radiationless decay of the excited triplet state ketone ($\text{T}_1 \rightarrow \text{S}_0$). In studies with the triplet aromatic hydrocarbons a striking dependence has been observed of the rates of radiationless decay on the $\text{T}_1\text{-S}_0$ energy separations and on the presence and the number of C-H groups in the molecule. The theory of the process appears to be well developed.³² An analogous effect could be operative here with the enhanced rate of the $\text{T}_1 \rightarrow \text{S}_0$ reaction proportional to the number of effective bonds in the molecule into which an appreciable fraction of the electronic energy ultimately flows as vibrational excitation. Such a proposal would appear to be consistent also with the observed temperature dependence of ϕ_{II} . If one takes the lowering of ϕ_{II} for the $n\text{-C}_3\text{H}_7\text{COR}$ ketones with variation of R from C_2H_5 to the more highly branched radical as a measure of the quantum efficiency of the $\text{T}_1 \rightarrow \text{S}_0$ process, then the temperature dependence of the ratio $\phi_{\text{II}}/\phi_{\text{T}_1 \rightarrow \text{S}_0}$ gives in theory the estimate of $E_{\text{II}} - E_{\text{T}_1 \rightarrow \text{S}_0} \cong 4 \pm 1$ kcal/mole for the ketones with ϕ_{II} temperature dependent. If $E_{\text{T}_1 \rightarrow \text{S}_0} \cong 0$, then $E_{\text{II}} \cong 4 \pm 1$ kcal/mole, in reasonable agreement with the 4.8- and 5.5-kcal/mole estimates derived earlier for this quantity. However, if this mechanism is assumed to be correct, one might expect a smaller but detectable temperature dependence to the $\phi_{\text{IIa}} + \phi_{\text{IIb}}$ values for the $n\text{-C}_3\text{H}_7\text{COR}$ ketones with $\text{R} = \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, n\text{-C}_4\text{H}_9,$ and $i\text{-C}_4\text{H}_9$. This is not observed.

(2) A chemical interaction between the β -H atoms and the excited carbonyl group may be invoked. Possibly some unexpected type of weak bonding (~ 2 kcal/mole) may exist between β -H atoms and the excited carbonyl group. With this model the "bonding" results in the lowered reactivity of the excited state for process II, and the temperature dependence is a consequence of the "bond"-breaking necessary to effect the other reactions of the excited state.

(3) Alternatively one might propose that the effect arises in the occurrence of a carbonyl abstraction reaction involving the β -H atoms. In this case it must be argued that the diradical formed, $\cdot\text{CH}_2\text{CR}_2'\dot{\text{C}}(\text{OH})\text{R}$, may lead to a cyclopropyl alcohol for only the very mild conditions which are not normally employed. It is demanded that the radical return usually to the original ketone by H-atom transfer with the net result of internal conversion of electronic energy. The fragmentation of the radical to form $\text{CH}_2=\text{CR}_2'$ and $:\text{C}(\text{OH})\text{R}$ or RCHO would have to have a significantly higher energy barrier and/or a lower A factor than that for the analogous reaction considered for the type-II process so that fragmentation could not be favored for normal conditions. Minor products attributable to the decomposition reactions of such an intermediate have been accounted for by β -H atom abstraction in several studies.³³ However, in the case of methyl isopropyl ketone

where the evidence for its occurrence at 2537 Å seemed most significant,^{33d} it has been shown recently that this type of rearrangement is an unimportant source of acetaldehyde and propylene products.³⁴

Obviously further definitive work will be necessary to allow a choice between alternative explanations of the interesting α -alkyl substituent effect observed here.

(c) **An Empirical Rule Relating ϕ_{II} to Molecular Structure in the $n\text{-C}_3\text{H}_7\text{COR}$ Ketone Photolysis at 3130 Å.** The previously observed relations between ϕ_{II} and molecular structure can be summarized by the empirical equations

$$\phi_{\text{IIa}} + \phi_{\text{IIb}} = [0.252(0.78)^m + 0.038n][e^{-1.9p/RT}/e^{-2.25p}] \quad (1)$$

$$\phi_{\text{IIa}}/\phi_{\text{IIb}} = (N_a A_a/N_b A_b)e^{-\Delta E/RT} \quad (2)$$

The first term of eq 1 formulates the effect of α -alkyl substituents on ϕ_{II} , and m represents the number of alkyl substituents attached to the α -carbon atom of the R group. The second term increases the calculated ϕ_{II} values for the case of ketones with *sec*-H atoms in the γ position; n is the number of these atoms. Depending on the interpretation of the reactive state involved in this case, the second term may either be related to the additional olefin product from singlet excited state participation in the type-II process or to an enhanced triplet reactivity for this case. (Presumably a third term would be necessary in the sum within the first brackets of eq 1 to account for tertiary H atoms in the γ position.) The exponential term of (1) introduces a temperature dependence to the ϕ_{II} values for the highly substituted ketones; $p = 1$ when there are two or more alkyl substituents on the α -carbon atom, and $p = 0$ for all other cases.

Equation 2, which defines the ratio of $\phi_{\text{IIa}}/\phi_{\text{IIb}}$, is presumably related to the ratio of the competitive rate constants for abstraction of γ -hydrogen atoms. $\Delta E = 0$ for those cases in which the two sources of process II

Table III. Comparison of Measured ϕ_{IIa} and ϕ_{IIb} Values from the 3130-Å Photolysis of the $n\text{-C}_3\text{H}_7\text{COR}$ Ketones with Those Calculated from Eq 1 and 2

R	Temp, °C	ϕ_{IIa}		ϕ_{IIb}	
		Exptl	Calcd	Exptl	Calcd
CH_3	58-151	0.252	0.252
C_2H_5	62-151	0.203	0.197
$n\text{-C}_3\text{H}_7$	61-151	0.106	0.099 ^a	0.106	0.099 ^a
$i\text{-C}_3\text{H}_7$	150	0.155	0.154
	100	0.112	0.116
	60	0.085	0.085
$n\text{-C}_4\text{H}_9$	150	0.035	0.034 ^b	0.248	0.240 ^b
	150	0.035	0.066 ^a	0.248	0.206 ^a
	110	0.029	0.029 ^b	0.243	0.244 ^b
	76	0.024	0.025 ^b	0.237	0.248 ^b
$i\text{-C}_4\text{H}_9$	75-150	0.055	0.066 ^a	0.151	0.131 ^a
	$sec\text{-C}_4\text{H}_9$	150	0.062	0.077 ^a	0.061
110		0.052	0.060 ^a	0.052	0.060 ^a
75		0.039	0.047 ^a	0.039	0.047 ^a
$t\text{-C}_4\text{H}_9$	150	0.118	0.120
	110	0.093	0.093
	75	0.073	0.074

^a Calculated from eq 1 and 2 assuming $A_a = A_b$. ^b Calculated assuming $A_a = 0.44A_b$.

(32) (a) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962, (1962); (b) *ibid.*, **38**, 1187 (1963); (c) G. R. Hunt, E. F. McCoy, and I. G. Ross, *Australian J. Chem.*, **15**, 591 (1962); (d) W. Siebrand, *J. Chem. Phys.*, **44**, 4055 (1966).

(33) (a) See ref 3, p 384; (b) F. E. Blacet and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **74**, 3382 (1952); (c) F. E. Blacet and R. A. Crane, *ibid.*,

76, 5337 (1954); (d) A. Zahra and W. A. Noyes, Jr., *J. Phys. Chem.*, **69**, 943 (1965).

(34) W. A. Noyes, Jr., and D. Roscher, private communication.

involve the same type of γ -H atom, *e.g.*, primary H atoms. For the one other case observed in this study, that for primary H atoms in the n -C₃H₇ group and secondary H atoms in the R group of the n -C₃H₇COR molecule, $\Delta E = 1.3$ kcal/mole. Presumably a slightly higher value would apply for the case of t -H atoms in the γ position of the R group. N_a and N_b are the numbers of γ -H atoms of a given type in the n -C₃H₇ and R groups, respectively, and A_a and A_b are the preexponential factors related to the rate constants k_{IIa} and k_{IIb} , expressed as a rate per γ -H atom. Unless some peculiar geometrical configuration favors the type-II process or the singlet state is involved significantly as well as the triplet, one would expect $A_a = A_b$. With the exception of the n -butyl n -propyl ketone case this assumption seems warranted. It is gratifying but perhaps not surprising that an equation with so many parameters fits all of the data well. Compare the experimental and calculated values of ϕ_{IIa} and ϕ_{IIb} in Table III.

One may predict ϕ_{II} values for the 3130-A photolysis of some ketones not yet studied through an extrapolation

of eq 1 and 2. Thus 4-nonanone, 4-decanone, etc., should have ϕ_{II} values equal to those for 4-octanone photolysis at 3130 Å: $\phi_{IIa} \cong 0.035$, $\phi_{IIb} = 0.25$ (150°); $\phi_{IIa} \cong 0.024$, $\phi_{IIb} \cong 0.24$ (76°). Furthermore, one expects for 2,2-dimethyl-4-heptanone that $\phi_{IIa} \cong 0.05$ and $\phi_{IIb} \cong 0.15$, independent of temperature. For 7-methyl-4-octanone one anticipates that $\phi_{IIa} \leq 0.04$ and $\phi_{IIb} \geq 0.25$.

Obviously the type-II process involves a complex interaction of many structural effects, a few of which may be identified in this work. It is hoped that further studies of this sort will help delineate further the relations between the photochemistry and the molecular structure of the ketones.

Acknowledgment. The authors are grateful for the support of this work through a research grant from the National Center for Air Pollution Control, Bureau of Disease Prevention and Environmental Control, U. S. Public Health Service, Bethesda, Md. We wish to acknowledge the significant constructive criticism of the original manuscript by Drs. P. Ausloos, T. J. Dougherty, W. A. Noyes, Jr., R. Srinivasan, and P. J. Wagner.

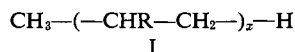
Stereochemical Equilibrium in Chain Molecules

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Abstract: A general theory of stereochemical equilibria in chain molecules possessing two or more asymmetric centers is presented. It is applied to vinyl polymers $\text{CH}_2-(\text{CHR}-\text{CH}_2)_x-\text{H}$ and their low molecular homologs in the presence of a catalyst capable of effecting racemization of the $-\text{CHR}-$ centers. The relative abundance of each stereoisomeric species is proportional to the sum of the statistical weights for all of its rotational conformers, *i.e.*, to the statistical mechanical configuration partition function Z for the species. The relevant partition function Z for the equilibrated system is the sum of the Z 's for all stereoisomeric species. It is expressed without approximation in terms of statistical weight parameters for rotational isomeric states, with due account of neighbor effects. Equilibrium populations of various dyads, triads, and higher sequences are readily derived for chains of any length. The stereochemical configuration of a given unit in a chain of many units is shown to depend not only on the symmetries of its immediate neighbors, but also on centers many units removed. The theory departs therefore from the statistics for an Ising lattice with first-neighbor dependence. Dyad and triad compositions of dimeric and trimeric homologs cannot in general be construed as being representative of infinite chains, as is shown by trial calculations. In general, the statistical distribution of symmetries of consecutive asymmetric centers is neither Bernoullian nor Markoffian. Available experimental results are interpreted according to the theory.

A general treatment of the spatial configurations of vinyl polymer molecules of the type



was published recently by the author and his collaborators.¹ Local bond conformations were represented in the terms of the rotational isomeric state scheme, which has gained widespread usage in the analysis of spatial configurations of chain molecules.²⁻⁴ Each

(1) P. J. Flory, J. E. Mark, and A. Abe, *J. Am. Chem. Soc.*, **88**, 639 (1966).

(2) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press Inc., New York, N. Y., 1954.

(3) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," translated from the Russian edition by S. N. Timasheff and M. J. Timasheff, Interscience Publishers, Inc., London, 1963.

bond was accorded three rotational states in keeping with the character of the rotational potentials applicable generally to C-C bonds. Potentials affecting rotations about a given bond are strongly dependent on rotational states of bonds which are first neighbors, and this circumstance was rigorously taken into account.

In typical vinyl chains for which the substituent group R is of a size commensurate with or larger than Cl or CH₃, most of the configurations of the chain are subject to prohibitive steric overlaps. Those which are free of severe repulsions between nonbonded atoms or groups are comparatively few in number. Which of the mani-

(4) T. M. Birshtein and O. B. Ptitsyn, "Conformation of Macromolecules," translated from the Russian edition (1964) by S. N. Timasheff and M. J. Timasheff, Interscience Publishers Inc., New York, N. Y., 1966.