The Photolysis of 2-Fluorocyclohexanone in the 313-nm Region. The Elimination of Hydrogen Fluoride from Vibrationally Excited Fluorocyclopentane

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Abstract

The gas-phase photolysis of 2-fluorocyclohexanone at 313 nm and 120 $^{\circ}\mathrm{C}$ is reported. The primary dissociative step appears to be



The 1-fluoropentanediyl species can disproportionate to form the 1- and 5-fluoro-1-pentenes, or cyclize to form vibrationally excited fluorocyclopentane. The latter molecule either undergoes collisional stabilization or decomposes unimolecularly to give cyclopentene and HF. The half-quenching pressure for the latter reaction was 2 torr. The disproportionation-to-combination ratio for the diradical was found to be 1.2. Some brief preliminary experiments on the liquid-phase photolysis of 2-chlorocyclohexanone and 2-fluorocyclohexanone are also described.

Introduction

A brief report on the solution-phase photolysis of 2-fluorocyclohexanone (FCH) appeared in 1963 [1]. It seemed of interest to investigate the gasphase photolysis of the ketone with the expectation that the fluorodiradical formed in the decarbonylation process undergoes ring closure to vibrationally excited fluorocyclopentane. Before this molecule is collisionally stabilized, it can eliminate HF in a unimolecular process to form cyclopentene, provided that the pressure is low enough to permit the latter reaction to occur. Such an observation would also give further corroborative evidence for the intermediacy of diradicals in the photolytic decomposition mechanism of medium-ring alkanones. We also carried out some preliminary experiments on the liquid-phase photolysis of FCH and 2-chlorocyclohexanone (ClCH), and these are reported in the present paper.

Experimental and Results

ClCH was prepared by the chlorination of cyclohexanone or obtained commercially from the Aldrich Chemical Company. FCH was prepared from ClCH by the method of Cantacuzène and Richard [2]. The proton nuclear magnetic resonance spectrum of the distilled material showed the ¹⁹F-¹H coupling centered at $\delta = 4.9$ ppm (TMS = 0), and the geminal coupling constant was found to be 49 Hz, in good agreement with other values [3]. The remainder of the protons were between $\delta = 1.5$ and 2.8 ppm. Integration of the peak areas gave a ratio of 1.0 to 8.1, in good agreement with the expected value. The infrared spectrum of the FCH showed a strong absorption at 1715 cm⁻¹ for the carbonyl group, and a very strong absorption at 1080 cm⁻¹ due to the C-F stretching vibration [4].

Liquid-Phase Studies

These were quite brief and are discussed first. The objective was to determine the rearrangement products arising from the initial acyl-alkyl diradical without the complication of the decarbonylation process. The photolyses were carried out in rectangular spectrophotometer cells (volume 1.5 ml) with suprasil windows. Neat liquid and methanol solutions were employed. Analysis was carried out by gas chromatography using an 18% diethylene glycol succinate on chromasorb W column.

The photolysis of ClCH gave rise to two primary products in an approximately 9:1 ratio. The major product was cyclohexanone and the other one had an identical retention time to 2-cyclohexen-1-one. In methanol solution the photolysis of ClCH gave two products of equivalent magnitude. One was again cyclohexanone and the other was assumed to be the dimethyl ketal of ClCH. Anderson [5] has reported the isolation of the diethyl ketal as a major product in the photolysis of ClCH in ethanol. Since C-Cl cleavage was the only direct bond-rupture process at 313 nm, no further experiments were conducted with ClCH.

The photolysis of neat FCH gave only one observable product which was identified as cyclohexanone by gas chromatography coinjection. In methanol solution two additional products were obtained. The formation of one of them was almost completely eliminated when 1,3-pentadiene was present in the photolysis solution. De Mayo and coworkers [1, 6] have previously observed the formation of methylhexanoate, cyclohexanone, and methyl-6-fluorohexanoate in the photolysis of FCH in methanol.

Gas-Phase Studies

These were carried out in a conventional mercury and grease-free highvacuum apparatus. The volume of the cylindrical quartz photolysis cell was 2150 cm³, and it was housed in a variable-temperature air-bath furnace. The cell pressures of FCH were measured by a Pirani-type gauge (CVC Autovac, type 3294B) that was enclosed in an aluminum furnace held at 70°C. The Autovac gauge was calibrated with cyclohexanone. FCH pressures ranged from 0.5 to 3.0 torr in the experiments. Higher pressures of added inert gas (CO₂ or N₂) were measured on a Bourdon-type gauge (Wallace and Tiernan, type FA-141). A PEK 210 high-pressure unfiltered mercury lamp, in conjunction with a PEK 912 lamp housing, was used as the radiation source. (This lamp was also used in the liquid-phase studies.) Separation of the reaction products was effected by gas chromatography using a 25-ft Carbowax 6000 column. Eluted samples were then further analyzed on a Finnigan 1015 mass spectrometer. The spectra were taken at 70 eV.

The majority of the experiments were performed at 120°C. The products of the gas-phase photolysis of FCH were identified as CO, cyclopentene, 1-fluoro-1-pentene, 5-fluoro-1-pentene, and fluorocyclopentane. The four condensable products showed up as three major peaks, which we shall call A, B, and C, on the gas chromatogram. Only a pure sample of cyclopentene was available for characterization purposes. The shape of peak A varied depending upon the total pressure in the photolysis system. At lower pressures there was a partial splitting of the peak into two distinct components which we were not able to resolve completely while maintaining a convenient analytical method for the measurement of peaks B and C. At higher pressures peak A showed a decrease in size relative to peaks B and C. Under these conditions the areas of peaks A and B became more nearly identical (A was the larger), and peak C showed a distinct increase in size. These variations in peak areas are noted since they must be compatible with the product assignments that we make and the mechanism that we propose. The trailing portion of peak A displayed a gas chromatography retention time identical to cyclopentene. The mass spectrum of peak A showed all the major positive ions for cyclopentene [7] but with a fluorocarbon component (C_5H_9F , see following) which became more important at higher pressures. A C_5H_9F compound can possibly give rise to all the positive ions which originate from C_5H_8 ; however, it is important to note that cyclopentene exhibits a large parent ion at m/e = 68 which we observed in the mixture, while the loss of HF in the mass spectra of fluorohydrocarbons results in ion peaks of negligible intensity [8]. Cyclopentene was therefore one of the components in peak A.

The mass spectrum of peak B established the compound as 5-fluoro-1-pentene. The parent ion $C_5H_9F^+$ at m/e = 88 was 15% of the base peak at m/e = 55. This major ion results from the loss of the CH₂F group, which compares with the loss of the CH₃ group from 1-pentene [7]. The remainder of the fragmentation pattern was very similar to 1-pentene, for example, both spectra contained major positive ions at m/e = 55, 41, and 27, which can arise directly from the olefinic portion of either molecule. (A cautionary note about rearrangement ions is warranted, see parenthetic note at the end of footnote 1.) The evidence supports the conclusion that the F atom is not located at the 1 position in the compound. The F-containing positive ions, which were all of lesser intensity (< 20% of the base peak), at m/e = 73 (C₄H₆F⁺), m/e = 60 (C₃H₅F⁺), m/e = 59 (C₃H₄F⁺), and m/e = 47 (C₂H₄F⁺), are also consistent with substitution of the F atom at the 5 position.

The assignment of compound B as 5-fluoro-1-pentene allowed the assignment of the second component of peak A as 1-fluoro-1-pentene, and our interpretation of the mass spectrum of the mixture confirmed this.¹

The mass spectrum of compound C was compared to cyclopentane [7] and heptafluorocyclopentane [8]. The major fluorine-containing ions were at m/e = 60 (C₃H₅F⁺) and m/e = 59 (C₃H₄F⁺). For values of m/e = 55 and lower the spectrum correlated closely with that of cyclopentane, including the occurrence of the base ion peak at m/e = 42 (C₃H₆⁺). The parent at m/e = 88 (C₄H₉F⁺) was only 1% of the base peak. However, fluorine substitution can result in a very low abundance for parent ions; the parent ion peak for heptafluorocyclopentane is <0.1% of the base ion peak, C₃F₃H₂⁺ [8]. The evidence strongly supports the fact that compound C was fluorocyclopentane.

The experimental data are given in Table I where the photolysis products are given in terms of the gas chromatographic peak areas. Photolysis times

¹ We observed the parent ion at m/e = 88 (C₅H₉F⁺) and a major ion at m/e = 59 (C₃H₄F⁺); the latter compares with the major ion $C_3H_5^+$ from 1-pentene. Both positive ions can arise by loss of the C_2H_5 group. Other prominent ions which supported the assignment were observed at m/e = 73 (C₄H₆F⁺), due to loss of the CH₃ group, m/e = 42 (C₃H₆⁺) and m/e = 29 $(C_2H_5^+)$. It should be noted that the positive ions at m/e = 42 and m/e = 29 are of little significance in the mass spectrum of cyclopentene [7]. The parent ion at m/e = 88 was 26% the base ion peak at m/e = 42. This compares with the parent ion at m/e = 70 (C₅H₁₀⁺) from 1-pentene which is 32% of the base ion peak at m/e = 42 [7]. If the C₃H₆⁺ fragment ion arises in both cases from the nonolefinic portion of the molecule, we see strong evidence for the assignment of the F atom at the 1 position. (Note: Correlations between structure and mass spectra are fraught with difficulty due to rearrangement processes, and these problems have been discussed for olefins and the isomeric pentenes in particular [9]. Any discussion of the possible origin of positive ions in the cracking pattern from the olefinic or nonolefinic part of a molecule must be viewed with this reservation. However, the evidence is supportive of the assignments that we have made. A referee has suggested that because of mass discrimination a comparison of the literature magnetic sector [7] and quadrupole mass spectral assignments may be questionable. The relative intensities of all the ion peaks in our spectrum of a standard sample of cyclopentene agreed closely with the literature cracking pattern [7]. It should also be noted that the interpretation involves qualitative identification, and not quantitative measurement.)

			Areas of GC Peaks		Cuclonentene	Decomposition	
Experiment† Number			AB				c
	<u>Cell Pre</u> Ketone	1 Pressure, Torr one CO ₂ (N ₂)	Cyclopentene + 1-fluoro-1-pentene	5-fluoro-l- pentene	fluoro- Cyclopentane	Calculated (A - B)	Stabilization (D/S)
2	0.5		368	106	79	262	3.32
4	1.0		1,454	755	460	699	1.52
5	2.0	(63)	325	242	490	83	0.17
6	2.0	(187)	430	292	527	138	0.26
7	1.0		2,510	1,081	544	1,429	2.63
8	1.0		2,061	983	372	1,078	2.90
9	1.0		1,994	1,021	409	973	2.38
10	1.0		1,987	955	404	1,032	2.55
11	2.0		5,704	3,396	2,313	2,308	1.00
12	2.0		4,611	2,368	1,605	2,243	1.40
13	1.0		707	326	321	381	1.19
14	1.0		1,835	945	745	890	1.19
15	1.0		895	450	334	445	1.33
16	2.0	59	1,672	1,277	1,883	395	0.21
17	2.0	52	528	391	581	137	0.24
18	2.0	96	2,329	1,900	2,480	429	0.17
19	2.0		4,598	2,398	1,510	2,200	1.46
20	2.0	12	3,095	2,284	2,771	811	0.29
21	2.0	1.0	3,900	2,401	2,291	1,499	0.65
22	2.0	3.0	387	186	267	201	0.75
23	2.0	3.0	5,541	3,274	3,637	2,267	0.62
24	2.0	7.0	8,996	6,072	7,622	2,924	0.38
25	5.0	4.0	12,920	8,000	9,516	4,920	0.52
26	2.0	1.0	10,020	5,196	5,190	4,824	0.93
27	2.0	0.7	873	415	334	458	1.37
28	2.0		4,877	2,447	1,594	2,430	1.52
29	2.0	121	1,188	1,190	1,695	0	0.00
31	3.0		14,220	7,320	6,117	6,900	1.13
32	2.0		6,880	2,646	1,370	4,234	3.09
33	2.0	3.0	566	381	393	285	0.73
34	2.0	6.0	267	170	214	97	0.45
35	2.0	6.0	6,956	3,938	5,020	3,018	0.60
:6	2.0	3.0	8,500	4,380	4,936	4,120	0.83
37	5.0		9,958	4,430	2,322	5,528	2.38
38	2.0		5,312	2,828	1,640	2,484	1.50
39	2.0		4,180	2,463	1,634	1,717	1.05

TABLE I. Data for the photolysis of 2-fluorocyclohexanone in the gas phase.

^a All experiments carried out at 120°C except for runs 32–37 at 180°C and 38 and 39 at 30°C.

were varied so that there are substantial differences in the total amount of product formation from run to run. Assuming identical gas chromatograph sensitivities for all four compounds and that the rates of formation of the two fluoro-olefins are equal, one may calculate the cyclopentene formed. The ratio of cyclopentene to fluorocyclopentane gives the decomposition to stabilization (D/S) value in each experiment.

Discussion

Liquid-Phase Studies

In ClCH photolysis the observed products can arise via the following reactions:



However, the formation of cyclohexanone in the photolysis of FCH is not so readily explained. Based on the known work with acyclic chloroketones, C---Cl bond rupture is to be expected at 313 nm [10] but no analogous case for C—F bond rupture in acyclic fluoro-ketones has been reported [10]. With the relative bond strengths involved, D(C-CI) = 78 and D(C-F) = 114 kcal/mol, respectively [11], C-F bond breaking is not expected. Despite this, it appears that C-F bond breakage must be promoted in some manner in the liquid-phase system to account for the cyclohexanone formation. It is important to note that De Mayo [6] confirms our observations on the photolysis of FCH in methanol, including the formation of cyclohexanone. We can assume that the triplet state, which is a precursor to the α -cleavage process that leads to a ketene and the eventual formation of methyl-6-fluorohexanoate, is quenched by piperylene. Norrish type I reactions are widely known to proceed via triplet excited states in the photolysis of cyclopentanones and cyclohexanones [12]. Surprisingly neither De Mayo [1, 6] nor ourselves observed any photorearrangement of FCH to an alkenal, which might have been expected to be a major product [12].

Gas-Phase Studies

Our work shows that decarbonylation is the major reaction pathway in the gas-phase decomposition of FCH. Assuming diradical intermediates, the reaction scheme is as follows:

(5)
$$F^* + M \xrightarrow{s} F + M$$

(6a)
$$(\mathbf{F} \rightarrow \mathrm{CHF} = \mathrm{CHCH}_2\mathrm{CH}_2\mathrm{CH}_3$$

(6b)
$$\longrightarrow$$
 CH₂=CHCH₂CH₂CH₂F

The asterisk refers to a highly vibrationally excited intermediate resulting from C—C bond formation. Although only a sample of one of the four condensable reaction products was available for characterization purposes, we conclude that the identification of the other three products is well established. The relative changes in the areas of peaks A, B, and C when the pressure was varied are entirely compatible with the proposed vibrationally excited intermediate. It is also reasonable to assume that the two possible disproportionation reactions of the 1-fluoropentanediyl species, reactions (6a) and (6b), should be equally probable. There is no evident reason why one reaction should be favored over the other. In the photolysis of 2methylcyclohexanone Badcock [13] observed that the disproportionation of the diradical formed in the decarbonylation reaction gave a ratio of the *cis*- and *trans*-2-hexenes to 1-hexene of 1.09 ± 0.08 , based on fourteen experiments.

No reaction product was detected from the acyl-alkyl diradical formed in reaction (1). On the basis of previous gas-phase work with alkyl-substituted cyclohexanones [14, 15] it would seem reasonable to anticipate some aldehydic product. If the intermediate diradical is very short lived, reactions (1) and (2) can be written as

It has previously been pointed out by Srinivasan [16] that in the gas phase, where phototransformations can occur from higher vibrational levels of the electronically excited state, decarbonylation may be regarded in some cases as a single dissociative step. However, there is some difficulty with this assumption in that aldehyde was also not detected as a product in the liquid-phase work, while the ketene, which similarly arises from the α cleavage reaction, was observed. There may be some other undetermined factor which is operative in both phases that prevents the formation of aldehyde, or if it is formed, it is not readily detectable. We conducted material balance experiments for CO versus the sum of the four products given in Table I. In any particular run the CO was oxidized to CO_2 in a CuO furnace, and measured by gas chromatography. Assuming equal sensitivities for all the compounds, an average ratio of CO/Σ condensable products = 0.95 was obtained. If we assume the unimportance of any significant alkenal formation in the gas phase, the primary photodissociative process can essentially be written as reaction (7). Our work provides no evidence concerning the multiplicity of the electronically excited state that photodecomposes and whether singlet and/or triplet diradicals are involved in the succeeding mechanism.

The D/S ratios for reactions (4) and (5) are plotted versus reciprocal pressure in Figures 1 and 2. Figure 1 represents the data from Table I for runs involving only FCH, while Figure 2 is for the remainder of the experiments with added bath gas. The plots are entirely consistent with the competition between the collisional stabilization and the unimolecular decomposition of a vibrationally excited intermediate. Numerous cases of similar HF elimination reactions, where the exothermicity of the combination process exceeds the critical energy for the subsequent decomposition process, have been well documented for fluoroethanes [17–19] and fluoropropanes and fluorobutanes [20, 21]. We may estimate the average internal energy of the vibrationally excited species formed in reaction (3) at about 85 kcal/mole at 120°C. This estimate is based on Kim and Setser's



Figure 1. Decomposition-to-stabilization ratio versus reciprocal pressure (torr⁻¹) of FCH. ●-120°C; ▲-30°C; dashed line—see text.

[21] evaluation of the average energy of chemically activated 2-fluorobutane as 88 kcal/mol at 20°C, with allowance for the strain energy of the ring compound [22] and the temperature difference which is involved.² The "hot" 2-fluorobutane was formed by $CH_3\dot{C}HF$ radical and $\dot{C}H_2CH_3$ radical combination. The critical energy for the elimination of HF from 2-fluorobutane is 53 kcal/mol [21], and the threshold energies for several monofluoropropanes and mono-fluorobutanes center around 55 kcal/mol, determined by both chemical activation and shock-tube pyrolysis methods [20, 21]. Based on these values the vibrationally excited fluorocyclopropane probably contains approximately 30 kcal/mol of excess energy above the threshold energy for HF elimination, so that the unimolecular decomposition process can readily occur in competition with bimolecular collisional deactivation.

The simple expression $D/S = k_d/k_s P^{-1}$ is not obeyed exactly in Figure 1 in that the intercept is not equal to zero. We do not feel that this has any particular significance and there is no need to postulate that cyclopentene

² Further uncertainty in these estimates could be caused by carryover of excess energy from the photolysis step if the lifetime of the diradical is short enough. For unfiltered radiation a larger range of energies is involved.



Figure 2. Decomposition-to-stabilization ratio versus reciprocal pressure (torr⁻¹) of FCH + added gas. \bullet -added CO₂, 120°C; \blacktriangle -added N₂, 120°C; \circ -added CO₂, 180°C. Effective pressure = $P_{FCH} + 0.3P_{CO_2}$ (or $0.1P_{N_2}$).

is formed in a separate pressure-insensitive reaction. It should be remembered that the absolute values of the D/S ratios are dependent upon the relative gas chromatographic sensitivity factors for the four compounds. Evidently the intercept would be lower if cyclopentene were more sensitive than fluorocyclopentane (or 1-fluoro-1-pentene, or both) under our analytical conditions. Further, the calculated cyclopentene yield would be lowered if the formation of 1-fluoro-1-pentene was slightly preferred over 5-fluoro-1-pentene, and there is no a priori reason to assume that they are formed with exactly equal probability. Badcock's data [13] show an upper limit of 1.2 for one pathway over the other in the 2-methylcyclohexanone case. The dashed line in Figure 1 is based upon the assumption that there is some calibration factor to be applied that results in the theoretical line in accord with the simple D/S expression. It is noteworthy that the lower error limit of the eight experiments at 1 torr encompasses this zero intercept line. The two data points at 180° C are omitted from Figure 1 since the D/Sratios appear to be high, and the implied change in the unimolecular decomposition rate constant is much too large over the temperature range covered.

In view of the preceding discussion the line in Figure 2 is arbitrarily drawn through zero intercept. The pressures of the added bath gases have been adjusted to give an effective quenching pressure. Based upon FCH as unity, relative energy transfer efficiencies were taken as 0.3 for CO_2 and 0.1 for N_2 [23, 24]. Any adjustment in these relative efficiencies moves the data points laterally. In view of all the uncertainties the line drawn is probably the most reasonable interpretation of our experiments. With the scatter in the data plotted in Figure 2 it is not possible to conclude that there is any discernible tendency toward upward curvature at low pressures, which occurs if cascade deactivation begins to become evident [18, 19].

For a value of D/S = 1 we see a half-quenching pressure $P_{1/2}$ of about 2 in both Figures 1 and 2. Table II lists some typical $P_{1/2}$ values for the elimination of HF from several different "hot" compounds formed by the chemical activation technique. They were selected to show the range of values that can be expected by varying the average internal energy and the molecular size and weight of the chemically activated species. Benson and Haugen [26] were the first to clearly discuss the effect of the substitution of more effective, lower frequency C—F oscillators for C—H oscillators.

For comparative purposes we take the $P_{1/2}$ values of 2 torr in the present work and 0.5 torr for 2-fluorobutane formed by radical combination. Some factors would tend to cause a reversal in these values. Fluorocyclopentane has additional vibrational modes, including the low-frequency puckering (pseudorotation) mode; also we estimated earlier that the internal energy of the fluorocyclopentane was about 3 kcal/mol less. Both factors would

chemicany desivated compounds							
Compound	P1, Torr	Temp. ^O K	Bibliography				
CH3CH2F	150.0	363	18				
CH3CHF2	110.0	352	19				
CH2FCHF2	4.0	513	25				
CH2FCHF2	2.0	393	25				
CH3CHFCD3	6.0	293	21				
$(CH_3)_3 CF^a$	160.0	29 3	21				
CH3CHFCH2CH3a	10.0	293	21				
CH3CHFCH2CH3	0.5	293	21				
⊂ ^F	2.0	393	This work				

TABLE II. Half-quenching pressures for the elimination of HF from selected chemically activated compounds

^a Formed by methylene insertion into the primary and secondary C—H bonds of CH₃CHFCH₃; the average internal energy is approximately 20 kcal/mol greater.

tend to increase the relative lifetime of the "hot" fluorocyclopentane molecule and its probability for collisional stabilization. However, there are converse factors which tend to increase the relative unimolecular decomposition rate of the fluorocyclopentane over that for 2-fluorobutane. The HF elimination in fluorocyclopentane can be favored sterically when the hydrogen and fluorine atoms are held in a close to coplanar configuration for the four-centered syn-elimination. We may further adduce that the threshold energy for the elimination of HF from fluorocyclopentane is less than for the linear fluorobutane molecule. For comparison we note that the activation energies for the elimination of HBr in the pyrolyses of cyclopentyl-bromide and sec-butylbromide are 43.7 and 46.5 kcal/mol, respectively [27], which is a $\Delta E_a \simeq 3$ kcal/mol. This approximate difference will be reflected in the critical energies. The effect of the difference in energy barriers is also shown by the two fluorobutanes formed by methylene insertion in Table II, where there is a factor of 16 in the $P_{1/2}$ values.³ Again, comparing the bromides, $E_a = 41.5$ kcal/mol for the elimination of HBr from *tert*-butyl bromide [27] which is a $\Delta E_a = 5$ kcal/ mol in favor of the enhancement of the decomposition rate for the tertiary-substituted compound. A similar difference of $\Delta E_a = 5$ kcal/mol exists for the secondary and tertiary butyl-chlorides [27].

We see therefore that the $P_{1/2}$ value presented here for "hot" fluorocyclopentane is generally consistent with existing data, and provides further confirmation of the validity of our interpretation of the experimental results.

The interpretation also provides further substantiation for the role of diradical intermediates in medium-ring alkanone photochemistry. This was previously questioned [16], but it is now widely accepted and generally established. Some original and compelling evidence was presented in 1964 [28] where a complete lack of stereo-selectivity in the decarbonylated ring-closed combination product 1,2-dimethylcyclopentane was reported in the gas-phase photolysis of cis- and trans-2,6-dimethylcyclohexanone. Free radicals also undergo disproportionation reactions, and the observation of disproportionated products from the alkyl-alkyl diradicals provides further basis for the existence of the diradical intermediates. In Table III we list the values of disproportionation-to-combination ratios that are available from studies in which complete product analyses have been conducted. The observation that internal hydrogen abstraction is favored over cyclization has been noted previously [29, 30], and the value of 1.2 for FCH is consistent with this. The value is based upon the sum of the two products which result from the initial combination step [31]. There is some evidence for a small inverse temperature effect on the disproportionation-to-combination ratio $(1.42 \pm 0.07 \text{ at } 30^{\circ}\text{C}, 1.17 \pm 0.19 \text{ at } 120^{\circ}\text{C}, \text{and}$

³ Configurational effects may also be involved.

	Disproportionation/Combination	n	Bibliography
Ketone Source	Products	Ratio	
2,6-dimethylcyclohexanone	2-heptene 1,2-dimethylcyclopentane	2.5	14
2-methylcyclohexanone	lcyclohexanone cis- and trans-2-hexene + 1-hexene methylcyclopentane		13
Cyclohexanone	l-pentene cyclopentane	1.7, 2.6	29, 30
2-fluorocyclohexanone	1- and 5-fluoro-1-pentene cyclopentene + fluorocyclopentane	1.2	This work

TABLE III. Disproportionation-to-combination ratios for various pentanediyls.

 1.04 ± 0.13 at 180°C). Similar effects have been observed previously [13, 14, 32–35] for various radicals, and a fuller account will be given for hexane-1,5-diyl [13, 36].

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