Experimental Section[5]

2-Methyl-2-ethoxy-1,3-dioxolane.—Ethylene glycol (96.0 g, 1.55 moles), triethyl orthoacetate (251.0 g, 1.55 moles), and 0.2 g of concentrated sulfuric acid were slowly heated, and 147 g of ethanol was recovered by distillation after 2 hr. Potassium carbonate (5.0 g) was added and the mixture was fractionated to give 117 g (57.1%) of 2-methyl-2-ethoxy-1,3-dioxolane, bp 140° (760 mm). The infrared and proton nmr spectra are consistent with the proposed structure.

Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.56; H, 9.13.

Methyl 2-Hydroxy-2-trifluoromethyl-3,3,3-trifluorobutanoate (IIIa).—Trimethyl orthoacetate (24.0 g, 0.2 mole) and hexafluoroacetone[6] (67.0 g, 0.4 mole) were heated in a stainless steel bomb at autogenous pressure for 6 hr at 150°. The crude product (84.3 g) was fractionated to give $CH_3OC(CF_3)_2OH$, bp 83° (760 mm), 30.7 g; and IIIa, 31.1 g (64.9%), bp 143–144° (760 mm). The infrared spectrum contained bands at 3.05 ($C(CF_3)_2$-OH) and 5.76 μ (ester C=O). The proton nmr spectrum showed a singlet at τ 3.56 (OH), a singlet at 6.31 (2 OCH_3), and a singlet at 7.21 (CCH_2C).

Ethyl 2-Hydroxy-2-trifluoromethyl-3,3,3-trifluorobutanoate (IIIb).—In a similar manner IIIb was prepared from triethyl orthoacetate and hexafluoroacetone (65.8%), bp 149° (760 mm), n^{25}D 1.3419.

Anal. Calcd for $C_7H_8O_3F_6$: C, 33.09; H, 3.17; F, 44.85. Found: C, 33.28; H, 3.18; F, 44.59.

Methyl α-(1-Hydroxy-1-trifluoromethyl-2,2,2-trifluoromethyl-n-valerate (IIIc).—Similarly, IIIc was obtained from trimethyl ortho-n-valeranoate and hexafluoroacetone in 72.1% yield, bp

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(5) Proton resonance spectra were obtained with a Varian Associates A-60 spectrometer.

(6) Commercial hexafluoroacetone of 99.54% purity from E. I. du Pont de Nemours and Co. was used.

56° (4.8 mm), n^{25}D 1.3675. The infrared spectrum contained bands at 2.98 (OH) and 5.85 μ (ester C=O).

Anal. Calcd for $C_9H_{12}F_6O_3$: C, 38.30; H, 4.29; F, 40.40; mol wt, 282. Found: C, 38.40; H, 3.60; F, 40.59; mol wt (cryoscopic in benzene), 277.

4,4-Bis(trifluoromethyl)-3,5-dioxoheptyl 3-Hydroxy-3-trifluoromethyl-4,4,4-trifluorobutanoate (IV).—2-Methyl-2-ethoxy-1,3-dioxolane (39.6 g, 0.3 mole) and hexafluoroacetone (100.0 g, 0.6 mole) were heated in a bomb at 150° for 8 hr. The crude liquid product (139.0 g) was fractionated to give IV, 48.0 g (34.6%), bp 114° (9 mm), 233–234° (760 mm), n^{25}D 1.3498, nmr signals at τ 3.68 (singlet, OH), 5.53 (quartet, OCH_2CH_3), 7.05 (singlet, CCH_2COO), and 8.70 (triplet, CH_2CH_3). The infrared spectrum contained bands at 3.01 (OH) and 5.83 μ (ester C=O). The mass spectrum did not contain the parent ion but all the major fragments are in agreement with the proposed structure.
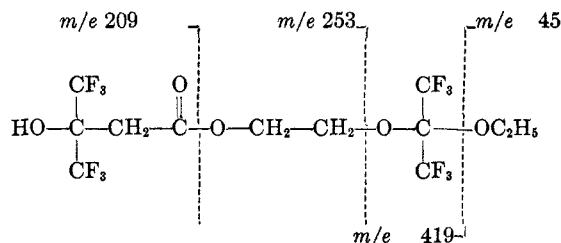
Anal. Calcd for $C_{12}H_{12}F_{12}O_5$: C, 31.05; 2.61; F, 49.11; mol wt, 464. Found: C, 31.17; H, 2.25; F, 48.80; mol wt (freezing point in benzene), 472.

The low-boiling product, bp 66–68° (9 mm), 5.9 g, could not be obtained analytically pure but the infrared and nmr spectra indicated that it is the intermediate $CH_3C(O)OCH_2CH_2OC(CF_3)_2$-$OC_2H_5$.

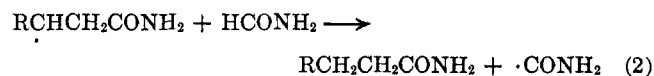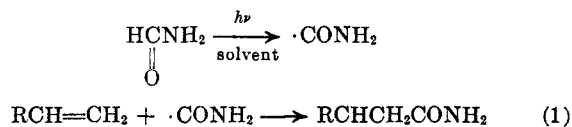# Ultraviolet and Electron Radiation Induced Addition to Olefins of Formamide

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Received April 8, 1966

Both the ultraviolet- and peroxide-induced addition of formamide to olefins has been reported in the literature.[1-3] For the ultraviolet-induced reaction, no quantum efficiencies were reported; for the peroxide-induced reaction, the efficiency was low. The purpose of our investigation was not only to determine the quantum efficiency of the ultraviolet-induced reaction but also to study the previously unreported electron-induced reaction. Both the quantum yield for the ultraviolet-induced addition and the G value for the electron-induced reaction were found to be low.

The sequence of reactions suggested by Elad and Rokach[1] is as follows.

$$\underset{\overset{\|}{O}}{HCNH_2} \xrightarrow[\text{solvent}]{h\nu} \cdot CONH_2$$

$$RCH{=}CH_2 + \cdot CONH_2 \longrightarrow R\underset{\cdot}{C}HCH_2CONH_2 \quad (1)$$

$$R\underset{\cdot}{C}HCH_2CONH_2 + HCONH_2 \longrightarrow$$
$$RCH_2CH_2CONH_2 + \cdot CONH_2 \quad (2)$$

Some experimental difficulties were associated with the investigation of the formamide–1-hexene system. For example, the 1-hexene is only sparingly soluble in formamide and thus the irradiation must be run either under conditions where one of the reactants is in great excess or where a mutual solvent is added to the system.

(1) D. Elad and J. Rokach, *J. Org. Chem.*, **29**, 1855 (1964).
(2) A. Rieche, E. Schmitz, and E. Gundermann, *Angew. Chem.*, **73**, 621 (1961).
(3) J. E. Allen, J. I. G. Cadogan, and D. H. Hey, *J. Chem. Soc.*, 1918 (1965).

Both methods were used. The solubilizing system was similar to that used by Elad and Rokach.[1]

For electron irradiation, both the rate of formation of heptanamide and the rate of disappearance of 1-hexene were measured. The simultaneous measurement of these two compounds permitted an estimate of the 1-hexene lost owing to side reactions. The results are expressed as G values (molecules formed or decomposed per 100 ev).

For the ultraviolet-irradiated systems the values for 1-heptanamide formation were always obtained while the 1-hexene content was determined in most cases.

Electron Irradiation Results.—Table I lists the G values for 1-heptanamide formation and for 1-hexene disappearance as a function of solvent and temperature. The results are averages for experiments conducted at 5, 10, 15, and 20 Mrads of radiation. At the highest dose, 30 to 60% of the 1-hexene originally present had disappeared.

The results may be summarized as follows: (1) the G values for 1-heptanamide formation are low, (2) re-

TABLE I
G VALUES FOR HEPTANAMIDE FORMATION AND 1-HEXENE DISAPPEARANCE

		Reactant and solvent, %				Mole ratio of formamide to 1-hexene	Temp, °C	G values for	
Sample	Formamide	1-Hexene	Acetone	t-BuOH	Dioxane			Heptanamide formation	1-Hexene disappearance
1	44.8	4.71	10.7	39.8	...	17.7	25	0.80 ± 0.05[a]	
2	50.3	5.21	...	44.5	...	18.0	25	0.82 ± 0.01[a]	
3	27.9	25.3	...	46.8	...	2.06	25	0.20 ± 0.02[a]	
4	45.6	4.76	10.5	39.3	...	17.9	18	1.09 ± 0.07	7.8 ± 0.3
5	48.6	5.06	46.3	...	...	17.9	18	1.42 ± 0.03	7.8 ± 0.6
6	38.0	3.49	...	...	58.51	20.3	18	0.44 ± 0.04	4.6 ± 0.5[b]
7	38.0	3.49	...	...	58.51	20.3	45	0.83 ± 0.02	4.0 - 7.6
8	45.6	4.62	...	49.78	...	18.4	15	1.27 ± 0.04	11.9 ± 0.0
9	45.60	4.62	...	49.78	...	18.4	45	1.86 ± 0.09	14.2 ± 0.5
10[c]	99.87	0.13	...	...	...	1.4×10^3	18	1.56	3.5

[a] These samples were not sealed and were subject to evaporative losses of both solvent and 1-hexene. [b] The rate of 1-hexene disappearance was not constant with dose and increased with increasing dose. [c] These values were obtained at 2.0 Mrads. At this level, 50% of the 1-hexene had disappeared with 44% of the reacted 1-hexene forming 1-heptanamide. At 20 Mrads, no 1-hexene was left in the system and the yield of 1-heptanamide was 60%.

TABLE II
ULTRAVIOLET IRRADIATIONS OF HOMOGENEOUS FORMAMIDE–1-HEXENE SYSTEMS

Run	Composition of reacn mixture, wt %				Molar ratio of formamide/ 1-hexene	Method	Irradiation time, hr	Heptanamide,[a] %	Heptanamide quantum yield, Φ
	Formamide	1-Hexene	Acetone	t-BuOH					
1	44.5	5.4	10.6	39.5	15.2	A (pyrex filter)	13.5	7.8	0.07
2		Same as run 1			15.2	A	13.5	8.8	0.08
3	41.9	1.7	10.5	45.9	50.0	B	10.0	23.3	0.08
4		Same as run 3			50.0	A (Corex filter)	10.0	18.2	0.06
5	45.9	1.7	5.3	47.1	45.4	A (Vycor filter)	10.0	22.4	0.07
6	47.8	1.8	10.1	40.3	50.0	C	1.0	21.2[b]	...
							2.0	22.1	...
							3.0	20.7	...
							4.0	19.7	...
							5.0	19.6	...
							6.0	18.9	...
7	48.2	0.7	10.2	40.6	84.0	C	1.0	32.7[b]	...
							2.0	33.5	...
							3.0	29.5	...
							4.0	30.0	...
							5.0	27.9	...
							6.0	25.3	...
8	48.5	0.4	10.3	40.8	250	C	1.0	46.9[b]	...
							2.0	41.2	...
							3.0	41.3	...
							4.0	41.1	...
							5.0	37.2	...
							6.0	32.1	...
9	44.8	4.7	10.7	39.8	17.6	D	6.0	13.0 (0.84)[c]	...
10	38.6	4.1	57.3	...	17.6	D	6.0	12.6 (0.81)	...
11	36.2	6.5	57.3	...	10.4	D	6.0	4.2 (0.47)	...

[a] Per cent theoretical yield based on 1-hexene consumed. [b] After 2 hr of irradiation, no 1-hexene was found in the solution. [c] Values in parentheses are total grams of heptanamide produced.

duction of the mole ratio of formamide to 1-hexene reduces the G value for formation of 1-heptanamide, (3) solvent effects on the G value for conversion to 1-heptanamide are unimportant for acetone and t-butyl alcohol but significant for dioxane (dioxane has been reported to react with terminal olefins[4]), and (4) the G value for 1-heptanamide formation increases with increasing temperature.

No effort was made to determine the side reactions responsible for the high G value for 1-hexene disappearance. However, reactions of addition, fragmentation, cross-linking, hydrogenation, and dehydrogenation on irradiation of olefins[5,6] are well documented in

the literature (Kharasch, et al.,[5] report a G value for disappearance of 1-hexene neat of 10.5 ± 0.5).

Ultraviolet Irradiation Results.—Several different methods were used for the ultraviolet irradiation. Again as in the case of electron irradiation, most of the irradiations were conducted in homogeneous systems. Using the uranyl oxalate[7] actinometer, we were able to derive approximate values for the quantum yield of heptanamide formation in 1-hexene–formamide systems. A partial listing of the results is given in Table II with the irradiation methods discussed in the Experimental Section.

The quantum yields for heptanamide formation listed in Table II are approximate, lower limit values.

(4) D. Elad and R. D. Youssefyeh, J. Org. Chem., 29, 2032 (1964).
(5) M. S. Kharasch, P. C. Chang, and C. D. Wagner, ibid., 23, 779 (1958).
(6) A. Charlesby, Proc. Roy. Soc. (London), A222, 60 (1954).
(7) W. G. Leighton and G. S. Forbes, J. Am. Chem. Soc., 52, 3139 (1930).

They were calculated on the basis of (1) the power output ratings given by the lamp manufacturer, (2) a measurement of the total intensity of the lamp in the wavelength region 310–450 mμ by uranyl oxalate actinometry, (3) absorption measurements of reaction mixtures in the region of 366 to 310 mμ, and (4) the assumption that only three wavelengths emitted by the lamp (366, 334.1, and 313 mμ) initiate the reaction. However, if the assumption is made that only the least intense line (334.1 mμ) emitted by the lamp initiates the reaction, an upper limit for Φ for heptanamide formation would be about 1.5.

An increase in the molar ratio of formamide/1-hexene did not affect Φ for heptanamide formation, but did increase the yield of heptanamide based on reacted 1-hexene, presumably by reducing the amount of 1-hexene consumed in side reactions with itself or the solvents. This is in general agreement with Elad and Rokach[1] but our data suggest a more critical dependence of yield on molar ratio.

In addition to the homogeneous systems discussed above, two-phase systems were photolyzed to eliminate the solvents which are sources of abstractable hydrogen and undoubtedly a hindrance to a possible chain mechanism. In these experiments small amounts (1 to 2%) of acetone were included as a sensitizer, and the upper 1-hexene phase was masked from the light to avoid reaction in this layer. The equilibrium solubility of 1-hexene in formamide was found to be 0.27% by weight or the mole ratio of formamide to 1-hexene was about 700 to 1. These conditions were the most favorable for avoiding excessive side reactions. Table III presents the data for these heterogeneous samples.

TABLE III

HETEROGENEOUS RUNS[a] ON ULTRAVIOLET-INDUCED ADDITION OF FORMAMIDE TO 1-HEXENE

Run	Compn mix, %	Total wt, g	Distance from lamp. in.	Time, hr	Heptanamide, %	1-Hexene, %
1	Formamide, 85.60		3.25	0.5	0.119	0.213
	1-Hexene, 13.54			1.0	0.089	0.219
	Acetone, 0.86	198.6		2.0	0.393	0.102
				4.0	0.839	0.234
				6.0	1.46	0.0426[b]
2	Formamide, 82.76		3.25	0.5	0.026	0.093
	1-Hexene, 13.10			1.0	0.073	0.137
	Acetone, 4.14	205.4		2.0	0.145	0.137
				4.0	0.264	0.130
				6.0	0.385	0.412
3	Formamide, 86.34		3.25	0.5	0.00	Trace
	1-Hexene, 13.66	196.9		1.0	0.00	Trace
				2.0	0.00	Trace
				4.0	0.00	0.253
				6.0	0.00	0.232

[a] See method E for experimental details. [b] The 1-hexene layer was almost entirely lost by volatilization.

Quantum yields were not obtained. It was found that (1) after a short induction period, the formation of 1-heptanamide is usually linear with time, and (2) although the presence of acetone is necessary for the formation of 1-heptanamide, increasing quantities of acetone suppress the formation of the amide.

Experimental Section

Electron Irradiations.—For all of the runs described with the exception of samples 1 to 3 in Table I, the system of preparation was as follows. A master batch of each composition was prepared, and 5 ml of the solution was added to a 10-mm o.d. tube. The contents of the tube were evacuated at −196° to 0.3 mm and sealed immediately to avoid any volatilization of the 1-hexene.

The sealed samples were then irradiated on a temperature-controlled plate with 2.0 Mev electrons from a Van de Graaff electron accelerator. Dosimetry was accomplished by using both the technique of Henley[8] and that of Dragonic.[9] The total dose was delivered at 1.0 Mrad per pass with 3 min between each pass under the electron beam. Analyses were accomplished using an Aerograph Model 200 thermal conductivity glpc with a column loading of 20% Carbowax 4000, terminated with terephthalic acid, on Analabs ABS 60–70 mesh support. The column was 0.125 in. in diameter and 72 in. in length. The heptanamide response of the detector was determined from an authentic sample of n-heptanamide with di-n-butyl maleate used as an internal standard for analysis. For the 1-hexene determinations, methyl isobutyl ketone was used as the internal standard.

Ultraviolet Irradiations.—For the ultraviolet irradiations, a number of different apparati and techniques of both irradiation and of 1-hexene addition were used. The method of analysis was the same as that described in the electron-irradiation section. The methods of irradiation were as follows with these letter assignments used in Tables II and III.

Method A.—The light source was a 100-w, high-pressure mercury lamp (Hanovia SOL 608A-36) filtered through Pyrex (Pyrex 7740, cutoff at 280 mμ, 50% transmission at 310 mμ). Other filters used were (1) Vycor 7910, cutoff at 210 mμ, 50% transmission at 240 mμ, and (2) Corex 9700, cutoff at 260 mμ, 50% transmission at 290 mμ. The apparatus consisted of a water-cooled quartz immersion well fitted into a Pyrex reaction cell by means of a standard tapered 60/50 $\mathbf{T}$ joint. The cell was constructed with side arms for N_2 flushing and making additions of 1-hexene. The volume of solution required for complete coverage of the lamp was about 200 ml, and the path length of light through the reaction mixture was about 0.5 cm. All constituents were added in the proportions indicated with the exception of 1-hexene. Following the procedure of Elad and Rokach,[1] the 1-hexene was initially added at 10% of the final total, with the remainder being added 10% at a time in a small amount of t-butyl alcohol–acetone solvent at 45-min intervals. A nitrogen stream was passed through the reaction system both during the irradiation and during the olefin addition. At the same time, the reaction vessel was partially cooled by tap water at 20° both from circulating through the condenser and through the jacket surrounding the high-pressure lamp.

Method B.—In this procedure N_2 flushing of the total reaction mixture was dispensed with. Instead, the reactants were separately flushed and immediately mixed. Additions of previously flushed 1-hexene were accurately pipetted into the reaction mixture as the reaction proceeded. The system described in method A was used.

Method C.—A 1200-w, high-pressure mercury arc lamp (Hanovia LL189A) with an internal Vycor and external Corex sleeve was mounted vertically. Pyrex tubes (10 mm in diameter) evacuated and sealed in the same manner as described for the electron irradiation were used and placed 2 in. from outer sleeve of lamp. The lamp was prewarmed to a constant output before removing the covering sheath.

Method D.—The same system was used as in C except the samples were placed in 38-mm diameter Pyrex tubes, nitrogen flushed, and stoppered. The distance from the lamp was about 2 in.

Method E.—The same system was used as in D but a stirrer was placed at the interphase in the hetrogeneous system, and samples were taken during the reaction by means of a stopcock at the bottom of the tube. The upper 1-hexene layer was shielded during the irradiation. Ultraviolet irradiation was accomplished using the apparatus described in method C.

(8) E. J. Henley and D. Richman, *Anal. Chem.*, **28**, 1580 (1956).
(9) I. Dragonic, *Nucleonics*, **21**, 33 (1963).