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Report On

EFFECT OF GAMMA RADIATION ON THE
REACTIONS OF SOME UNSATURATED ORGANIC COMPOUNDS

by

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ABSTRACT

The effect of radiation on several reactions of unsaturated organic compounds was studied. The summary of experimental studies and results is as follows.

The addition reaction of hydrogen sulfide to olefins showed a substantial effect. The effect on the reaction of hydrogen sulfide and propylene was studied at a temperature of -78.5°C , varying compositions, dose rates, and times of radiation. The results of conversions and product analysis are reported.

Other studies included copolymerization of ethylene and propylene, reactions of acetylene alone and with ethylene and acetic acid and copolymerization of sulfur dioxide with allyl bromide, allyl chloride, hexene-2 and 2-methyl pentene-1. The reactions of acetylene were not successful. The effect on other reactions were substantial and the results are included in the report.

I. INTRODUCTION

This report covers preliminary investigations on the effect of gamma radiation on some reactions involving several unsaturated organic compounds. This work is an extension of previous work done in this laboratory and published elsewhere⁽²⁾.

The addition reactions between hydrogen sulfide and propylene, hexene-1, octene-1 and decene-1 were studied with emphasis on the addition reaction to propylene. The effect of radiation on mixtures of ethylene and propylene, and reactions involving acetylene alone and with ethylene and acetic acid, and the copolymerization of sulfur dioxide with allyl bromide, allyl chloride, hexene-2 and 2-methyl pentene-1 was also studied.

II. REACTIONS INVESTIGATED

A. Olefin-Hydrogen Sulfide Reactions

It is known that the addition of hydrogen sulfide to olefinic bonds takes place only under rather severe conditions. A number of workers have studied the reaction and have employed temperatures from 150°C to 750°C, various catalysts, and usually elevated pressures. Hydrogen fluoride, boron trifluoride, peroxide catalysts or silica-alumina catalyst etc. are used. In most cases the yields are low. The products are primarily mercaptans and sulfides, but complex by-products are also formed^(4,5).

The addition reactions also occur under the influence of light having a wavelength less than 3000Å⁽⁶⁾. The mechanism of the addition is described as one of a free radical

chain and is dependent upon the preliminary dissociation of hydrogen sulfide. This study was conducted to find the effect of gamma radiation on the addition reaction.

1. Preliminary Work

The preliminary work was conducted to find suitable olefins and optimum operating conditions, for a more detailed study. The olefins studied were propylene, hexene-1, octene-1, and decene-1. The reactions were carried out at -78.5°C , 0°C and ambient temperature. Glass vials were used at subatmospheric pressures, while at elevated pressures, steel reactors were used. The reaction vessels were irradiated at a dose rate of about 40 Krep/hr. for 0 to 40 hours. All the reactions were run with composition of 1:1 mol ratio of hydrogen sulfide and olefin. The reactions were followed by observations of odor change, volume change, pressure change or chromatographic analysis.

The reactions with hexene-1 and decene-1 were found to proceed very slowly at room temperature. Octene-1 reacted slowly at -78.5°C . The reaction with propylene was the most successful among the olefins tried. Since propylene would be expected to give less complex products than higher olefins, it was decided to first consider the addition reaction between propylene and hydrogen sulfide.

2. Further Experimental Work

As reported earlier in the section on preliminary investigations, the major emphasis during the work on olefin- H_2S reactions was on the propylene- H_2S reaction. The following

operating variables were selected as a result of preliminary data:

Temperature - -78.5°C

Composition - (a) 1:1 mol ratio propylene:
 H_2S

(b) 1:1.7 mol ratio propylene:
 H_2S

Radiation Time - 0 to 40 hours

Dose Rate - 40 to 80 Krep/hr.

At the temperature of -78.5°C , the vapor pressures of the reactants are below atmospheric pressure and hence a glass system is quite suitable. A description of the equipment follows this section.

(a) Equipment and Materials

The reaction vials were made out of 22 mm. diameter pyrex tubing. The upper end of the vial was constricted and a vacuum stopcock attached to the neck. The vials were approximately 8" in body length.

The loading system consisted of a glass manifold with two loading lines, two lines for vials, and a vacuum line. It is similar to the schematic drawing in Figure 6, Report No. 1943-4-60-P (2).

The reactants were of C.P. grade and used as supplied by The Matheson Co.. Hydrogen sulfide and propylene have minimum purities of 99.8 % and 99.0 % respectively. These same gases were used for the chromatography standards. Pure propyl mercaptan, sulfide and disulfide were used as supplied by Eastman Kodak Co..

(b) Experimental Procedure

(i) Loading

All loadings were done after evacuation to about 700μ . The loading was done by a two step condensation of the reactants. Each reactant was condensed in a graduated vial (from the gas tank) to make an exact measurement of the amount, and then transferred to the reaction vial by evaporation and condensation. This was done at dry ice temperature (-78.5°C) and liquid nitrogen temperature (-190°C). Throughout the whole process of loading, the pressure was sub-atmospheric and as far as possible, no air was allowed to enter the system.

(ii) Irradiation

The reaction vials were kept at constant temperature by placing them in Dewars with constant temperature mixtures cooled by dry ice. They were placed before the gamma source and radiated for fixed amounts of time. The dose rate was measured by employing the oxidation of ferrous sulfate solution in one case (2). This measurement was applied to find a correction factor on dose rates in air as found from charts available in the laboratory. The correction factor comes in as a factor for shielding by the glass reactor. The dose rates in other cases were then found by applying this correction factor and the charts described.

(iii) Product Recovery

After irradiation the unreacted materials were driven off by gradually raising the temperature of the vials from -78.5°C to room temperature. Any remaining dissolved reactants

will have a detectable effect in the analysis of the product on the chromatography unit. By connecting the outlet of vials to cold traps it was made certain that no appreciable amounts of products were lost by evaporation or entrainment. The products were collected and weighed.

(iv) Analysis of Products

Several methods of analysis were tried. The chromatography unit was found most suitable. The mass spectrometer and the infrared spectrometer data were fairly hard to interpret. In several cases fractionation was used as a preliminary step to further analysis.

A Fisher-Gulf Partitioner was used for analysis. The machine was operated at temperatures of 85°, 100°, and 140° depending upon the column used. Two types of column were tried. The first column was filled with 30-60 mesh ground firebrick on which tricresyl phosphate was deposited. The second column was filled with Tide (30-60 mesh). Helium was used as carrier gas in all cases.

Known samples of reactant gases and products were used to find the retention times for individual components in the various columns used.

3. Discussion of Methods and Results

The chromatography method for analysis of products will now be discussed. It was found that both tricresyl phosphate and Tide columns had respective advantages. The first column needed a temperature of 140°C for operation while the second column required a temperature of 85°C, to get suitable peaks.

The trailing effect was lower with Tide. However the reproducibility with Tide was lower compared to tricresyl phosphate column. This however, may be due to other experimental errors.

With known samples of propyl mercaptans and propyl sulfides, the chromatography analysis always showed lower mercaptan and higher sulfide percentage (error of about 3 %). The exact reason is not yet known. It may be due to volatilization of mercaptan. However, several other reasons are possible.

A linear correlation was found between the actual percent weight of mercaptan in a known sample and the one found on the chromatography unit.

A summary of results is given in Tables I and II and Figure 1.

The data presented on the propylene and hydrogen sulfide addition reaction is only a part of the intended study. Hence, no definite conclusions are made. However, the following is indicated:

Gamma radiation can induce the addition of hydrogen sulfide to olefins. The products obtained for addition reactions of hydrogen sulfide and propylene were primarily n-propyl mercaptan and n-propyl sulfide. The reaction proceeds at a moderate rate up to about 40 % consumption of hydrogen sulfide at 1:1 mol ratio of reactants and -78.5°C .

G values based on hydrogen sulfide, varied from 1800 to 95000. The lower G values may be wrong because of the presence of air. It was found that the yields were low for experimental runs conducted with the presence of slight amounts of air in the

TABLE I.
Summary of Reactions of H₂S and C₃H₆ Made at -78.5°C and
1:1 Mol Ratio of Reactants

(Millimoles H₂S charged = Millimoles C₃H₆ charged = 169)

Run No.	Dose Rate Krep/ hr.	Dose Krep	Irrad- ia- tion Time Min.	Weight of Pro- duct Gm.	Analysis of Product			Milli- moles of Mer- captan in Product	Milli- moles of Sul- fide in Product	Per- cent- age Con- ver- sion of H ₂ S	G
					Propyl Mercap Wt %	Propyl Sulfide Wt %	Wt %				
174270-1	40	89	133	0.831	60	40	6.54	2.81	5.5	8,280	
174270-2	40	160	240	1.436	80	20	15.08	2.43	10.4	8,820	
174270-3	40	398	598	1.056	64	36	8.83	3.24	7.1	2,430	
174270-4	40	600	899	1.323	75	25	13.26	2.65	9.4	2,130	
174272-1	40	1610	2430	5.576	61	39	44.66	18.38	37.2	3,150	
174272-2	40	1610	2430	3.867	76.5	23.5	38.83	7.68	27.5	2,330	
174272-3	63	127	121	4.070	67	33	35.98	11.28	24.5	30,700	
174272-4	63	1530	1458	5.153	61	39	41.23	17.02	34.5	2,900	
174273-1	63	355	338	5.687	65	35	48.58	16.80	39.5	14,800	
174273-2	63	1040	998	6.285	64	36	52.65	19.24	42.5	5,680	
174274-1	80	40	30	3.980	74	26	38.67	8.75	28.0	95,500	
174274-2	80	80	60	4.559	67	33	40.10	12.72	31.2	53,200	
174274-3	80	902	678	5.921	61	39	47.42	19.53	39.5	5,960	
174274-4	80	2560	1920	6.177	65.4	34.6	53.04	18.08	42.0	2,240	
174282-1	80	166	125	4.029	80	20	42.31	6.81	29.0	23,700	
174282-3	80	166	125	2.825	80.2	19.8	29.75	4.72	20.3	16,900	
174282-2*	80	166	125	0.308	89	11	3.59	0.28	2.3	1,860	

Note* Reactor radiated with slight amount of air inside.

TABLE II.

Summary of Reactions of H₂S and C₃H₆ Made at -78.5°C and with Varying Ratios of Reactants

Run No.	H ₂ S	Millimoles charged	Ratio (mole) H ₂ S: Propylene	Dose Rate Krep/hr.	Dose Krep	Irradiation Time Min.	Wt. of Product gm.	Analysis of Product		Mer- cap- tan in Pro- duct, Milli- mole	Sul- fide in Pro- duct, Milli- mole	Per- cent- age Con- version of H ₂ S
								Pro- pyl Merc. wt %	Prop. Sul- fide wt %			
174255-1	176	148	1.18:1	40	280	420	-	-	-	-	-	-
174256-A	122	75	1.63:1	40	660	989	0.426	76	24	4.25	0.865	4.2
174256-B	212	124	1.7:1	40	938	1398	3.178	66	34	27.6	9.15	17.3
174256-C	154	91	1.7:1	40	162	243	0.966	71.5	28.5	9.09	2.34	7.5
174258-1	156	91	1.71:1	40	120	180	Trace	-	-	-	-	-
174258-2	160	95	1.7:1	40	240	360	1.089	74.8	25.2	10.7	2.35	8.2
174258-3	156	91	1.71:1	40	400	600	2.963	76.1	23.9	29.6	6.02	20.9
174258-4	170	101	1.68:1	dark run	0	7200	0.000	-	-	-	-	-

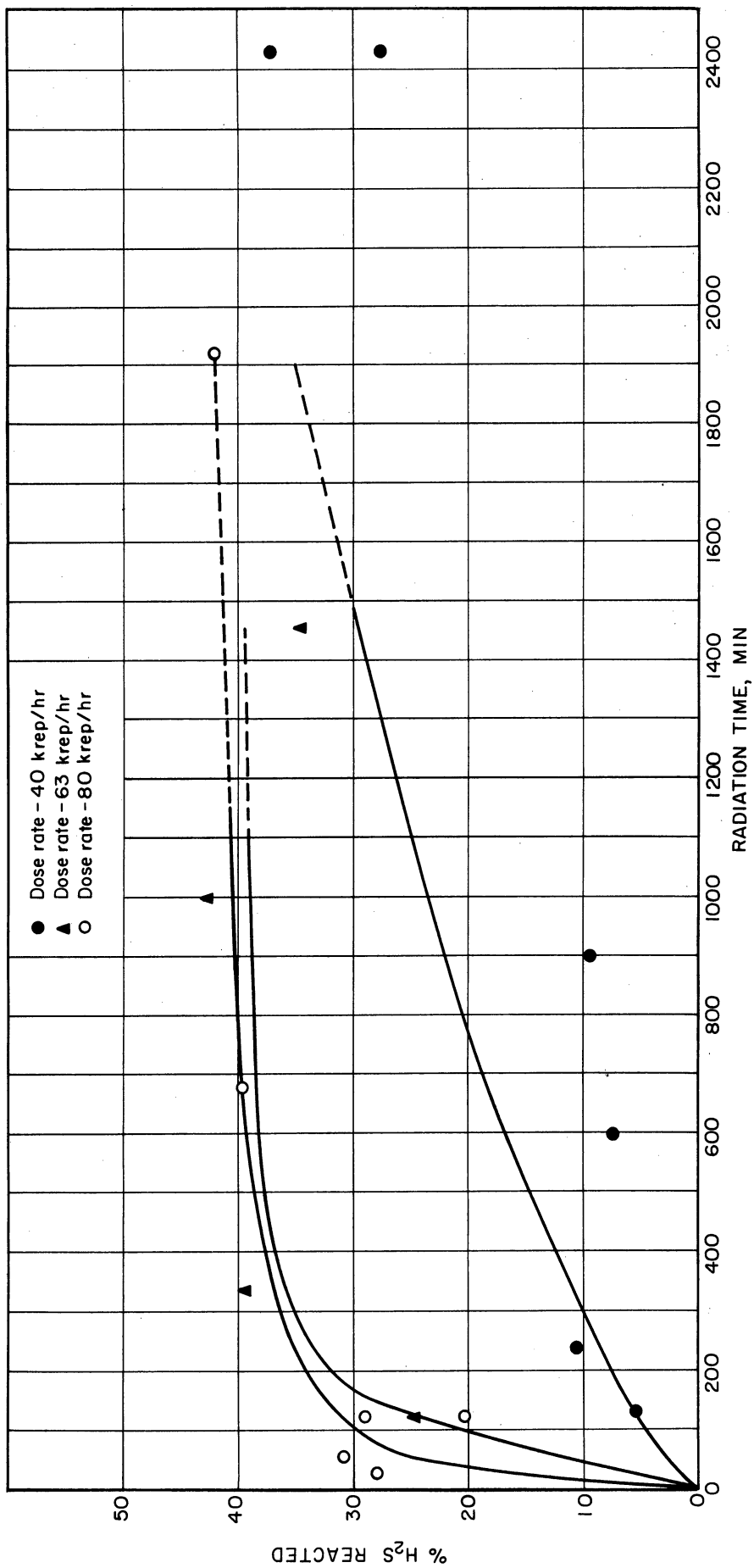


Figure 1. Addition of Hydrogen Sulfide to Propylene

reactor. This might indicate that the lower G values resulted from insufficient evacuation of the reactor before loading.

B. Miscellaneous Reactions

1. Ethylene-Propylene Copolymerization

Attempts were made to copolymerize ethylene with propylene in the vapor phase. After unsuccessful attempts at 20°C in glass vials one run was made at 2000 psig and 120°C in a steel bomb which yielded a viscous liquid product. The conditions are summarized in Table III.

Five runs differing only in the concentration of the reactants were made in the glass vials at 110 psig and 20°C. The vials, made of heavy-wall glass tubing, were first evacuated, then loaded at 20°C to 100 psig with the desired proportion of ethylene and propylene, and finally cooled to -78°C before being sealed. No reaction was observed during any of the runs in the glass vials.

In a further attempt to obtain a reaction in this system, one run was made in a high pressure Aminco bomb at initial conditions of 2000 psig and 120°C. The bomb was loaded with an equimolar mixture of ethylene and propylene to a pressure of 740 psig at 20°C and heated to 120°C before irradiation. A temperature of 100-120°C was maintained during the run. At the end of 140 hours of irradiation the pressure had dropped to 1850 psig at 120°C. A product consisting of 14.7 gm. of a viscous liquid was obtained.

No analysis was made of the liquid or gaseous products of any of the ethylene-propylene runs.

TABLE III.
Effect of Radiation on Mixtures of Ethylene and Propylene

Vial No.	Composition, mol % Ethylene	Propylene	Total Charge	Pressure psig	Temp. °C	Radiation Rate Krep/hr.	Radiation Time hrs.	Results
1	100	0	105 cc.	110	~20	~60	45	No observable products
2	0	100	105 cc.	110	20	60	45	
3	50	50	105 cc.	110	20	60	45	
4	25	75	105 cc.	110	20	60	45	
5	75	25	105 cc.	110	20	60	45	
Aminco bomb	50	50	444.5 gms.	2000 psig (0 hrs. 120°C) 1850 psig (140 hrs. 120°C)	100-120	15-20	140	Viscous liquid 14.7 gms.

2. Acetylene Reactions

Several runs with acetylene in various systems were made in an attempt to obtain radiation induced reactions. Reactions involving acetylene alone, acetylene with ethylene, and acetylene with acetic acid were attempted. The conditions of the five runs are given in Table IV.

All the reactions were conducted in a 1500 cc high pressure Aminco bomb fitted with a 340 psig blow-out disc. The pressure before and after each run was noted and the vessel was examined for evidence of products. No reaction was detected in any of the runs but since the initial weight of acetylene in the bomb was very small, no definite conclusions can be reached.

3. Olefin-Sulfur Dioxide Reactions

The work of Bray (1) on polysulfone production is being extended. Several preliminary runs have been made using three compounds which had been referred to as inhibitors by earlier workers. These compounds, allyl bromide, hexene-2, and 2-methylpentene-1 have all been found to copolymerize with SO_2 at appropriate temperatures under gamma radiation. Allyl chloride, which is known to react with SO_2 , copolymerized rapidly even before irradiation. This was probably due to impurities in the system. Neither allyl bromide nor 2-methylpentene-1 showed any noticeable reaction when irradiated at 20°C but both gave appreciable yields of polymer at -78°C . One of the two hexene-2 runs showed some polymerization during the warming up period between loading at -78°C and irradiation at 20°C . There was, however, no apparent additional reaction induced by the radiation. The other sample

TABLE IV.
Effect of Radiation on Acetylene Reactions

Run No.	Components	Pressure psig	Temp. °C	Radiation		Remarks
				Rate Krep/ hr.	Time hrs.	
1	Acetylene	25	~ 25	15-20	168	No observable products, fishy smell.
2	Acetylene-dissolved in 25 cc. of acetone	10	~ 25	15-20	100	No observable products.
3	suspended on asbes- tos.	25	~ 25		100	No observable products.
4	Acetylene 25 mol % Ethylene 75 mol %	85	~ 25	15-20	85	No observable products.
5	Acetylene gas phase 1500 cc. bomb connected to a glass vial containing 5 cc. acetic acid.	10	~ 25	15-20	40	No observable products.

was irradiated at -78°C and showed no obvious reaction even after standing at room temperature for several days. The vial containing this sample has not yet been opened and it is possible that some polymer is present but dissolved in the monomer- SO_2 solution. Attempts were also made to polymerize allyl chloride, allyl bromide, and 2-methylpentene-1 alone, without the presence of SO_2 . Only in the allyl chloride run was any evidence of reaction visible.

III. CONCLUSIONS AND PROPOSALS FOR FUTURE WORK

The results obtained for the addition reaction of hydrogen sulfides to olefins show a substantial effect of radiation on the reaction. The effect on the propylene-hydrogen sulfide system will be studied further from the viewpoint of kinetics and mechanism. Other olefins may also be investigated.

No further work is planned on reactions involving acetylene or on ethylene-propylene copolymerization.

The work on polysulfone reactions is being extended to include diolefins and cyclo-olefins. Kinetic studies are planned for a somewhat later date.

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