AD A117158

LASER INDUCED POLYMERIZATION REACTIONS
IN SOLID PROPELLANT BINDERS (U)

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INTRODUCTION

The use of organometallic compounds to catalyze urethane reactions between polyols and isocyanates has found extensive use in many industrial and military applications. Organometallic compounds are used as catalysts in the processing of solid propellants to accelerate the curing reaction of the binder in systems where crosslinking involves urethane formation between a prepolymer with hydroxyl groups and polyisocyanates.

It has been observed that simple alcohol-isocyanate reactions are susceptible to photochemical enhancement when exposed to a low intensity tungsten light source (1). This photochemical rate enhancement of urethane formation occurred in dilute solutions of carbon tetrachloride both in the presence and absence of organometallic cure catalysts. However, the rapid polymerization of polyols with isocyanates requires the presence of an organometallic catalyst; thus, the concept of photoassisting the reactivity of these catalysts appeared to be an interesting area of investigation. Consideration of this phenomenon prompted the idea that a high energy monochromatic radiation source might be useful in promoting specific chemical reactions and better controlling the cure process of urethane reactions.

This effort examines the effect of ultraviolet and visible laser radiation in conjunction with various organometallic catalysts on the formation of propellant binders. Laser controlled reactions may proceed by pathways not encountered under thermal or other photochemical conditions. Also, the laser has the advantage of providing an intensely concentrated monochromatic beam which allows polymerization to occur at ambient temperature rather than at elevated temperatures. The potential use of the laser as a polymerization tool may provide greater control over the reaction process.

The work described here was initiated to determine the effects of laser radiation on the condensation reactions of polyols and isocyanates and to assess the influence of small concentrations of photoabsorbing

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additives. Several classes of organometallic compounds known for their ability to catalyze these types of reactions were screened using ultraviolet lamps. Of these, several compounds were found to be particularly receptive to photoactivation in these reactions and were subjected to detailed laser investigation. The results of monochromatic radiation on these photocatalyzed reactions at 266, 365, and 532 nm are reported here.

EXPERIMENTAL

All experimental samples were prepared by the following procedure: A sample of the organometallic compound was placed in a small mortar and ground with a pestle until the material was finely divided. One milligram of the organometallic compound was added to 4.25 ml of isophorone diisocyanate (IPDI). The sample was then thoroughly mixed by shaking for one-half hour on a mechanical shaker.

1.41 ml of the IPDI/organometallic mixture was combined with 10 ml of polyethyleneglycol adipate (PGA) and thoroughly mixed. The samples were then evacuated in a glass vacuum desiccator to remove dissolved air and then opened to the atmosphere. Some samples were run under a nitrogen or oxygen atmosphere. In these cases, the appropriate gas was used to return the samples to atmospheric pressure. An aliquot of each sample was transferred to an ultraviolet 10 mm cell for irradiation. Also an aliquot of each sample was used as a reference standard. At various time intervals, viscosity measurements were made on both the control and irradiated samples. During irradiation, the sample holder was continuously moved up and down in a vertical motion by a mechanical device to expose the entire sample to the laser beam.

All samples that were run in these experiments had an NCO/OH ratio of 1.0 and contained 0.0025 weight percent catalysts. Therefore, to maintain the same ratio, experimental samples containing hexamethylene diisocyanate (HMDI) were prepared in a similar manner to those with IPDI. Thus, only 3.3 ml of HMDI were mixed with 1.0 mg of the organometallic catalyst and then 1.07 ml of this mixture was added to 10 ml of PGA polymer to make the final sample for irradiation.

BLAK-RAY ultraviolet lamps having wavelengths of 254 and 366 nm were used in the preliminary screening of the organometallic compounds shown in Table I. Those samples which showed increased reactivity were then selected for laser testing. A Quanta-Ray Model DCR Nd:YAG laser system was used as the source of irradiation in these experiments. This DCR Nd:YAG laser provided 220 mJ/pulse at 532 nm, 115 mJ/pulse at 355 nm, and 50 mJ/pulse at 266 nm. In all the experimental reactions reported in this paper, the laser was operated at 10 pulses per second.

The Ferranti-Shirley Viscometer System was used to follow the rate of reaction of the diol prepolymer with the diisocyanate by measuring the change in viscosity as a function of time.

A Beckman Model ACTA MIV spectrophotometer was used to obtain spectra

of the catalysts listed in Table II. The catalysts were used as received. Solvents used were spectroquality solvents. The solvent for ferrocene was 2,2,4-trimethylpentane. Dibutyltin diacetate solution was prepared using acetonitrile as solvent. Molar absorbtivities at 266 and 355 nm for 1,1'-ferrocenedicarboxylic acid were obtained with a methanol solution, and the molar absorbtivity at 532 nm was obtained in an acetone solution. The remaining spectra were obtained using methanol as solvent.

The preliminary screening of approximately sixty organometallic compounds indicated significant photoactivity occurred in about ten percent of the samples tested. Six samples were selected for closer examination and controlled exposure to intense monochromatic ultraviolet and visible laser irradiation. The results of these experiments are given in Tables II and V.

RESULTS

These investigations showed that ultraviolet and visible irradiation of catalyzed gumstock mixtures of polyethyleneglycol adipate (PGA) and various isocyanates could significantly increase the rates of urethane bond formation. However, the laser enhanced reaction rate was found to occur only when specific organometallic catalysts were present at the wavelengths used. This secondary acceleration in rate is over and above the already increased rate of reaction found to occur with these catalysts under nonphotolyzed conditions. At the wavelengths investigated the greatest acceleration occurred when the organometallic compounds contained iron. Most other metal containing compounds were found to produce lesser or no photorate enhancement.

Two ultraviolet lamps were employed to assist in the rapid screening of a wide variety of candidate organometallic catalysts. One lamp produced low intensity radiation at 254 nm and the other at 366 nm. These lamps permitted several samples to be simultaneously irradiated. The possible effect of photoactivity on the hydroxyl-isocyanate reactions of PGA, IPDI and various organometallic compounds was determined. After a minimum of two hours exposure, the viscosity of each sample was measured and compared with its appropriate reference sample. Those samples which showed the greatest viscosity differences were selected for further investigation with the laser. The results of these initial screening tests are shown in Table I. These viscosity differences between the irradiated and control samples were taken to be a direct measurement of the enhanced polymerization reaction.

The data presented in Table II show the actual viscosities observed, as a function of time, when identical PGA and HMDI or IPDI samples containing 0.0025% catalyst by weight were irradiated with a pulsed Nd:YAG laser. The laser enhanced reactions were observed to be extremely sensitive to the concentration of catalyst employed. When concentrations of catalyst were doubled from the 0.0025% level, the viscosity increased

beyond the limit of the viscometer within 30 minutes. Solvents were not employed to avoid possible complications due to extraneous solvent-assisted charge transfer complexes which might affect the reaction mechanism.

A cursory examination was made to determine if the reactivity of a linear aliphatic isocyanate (HMDI) differed from that of a cyclic aliphatic isocyanate (IPDI) in these reactions. The data obtained do not show any reaction enhancement or inhibition trends which could be directly attributed to a photocatalyzed reaction pathway favoring one isocyanate form over the other.
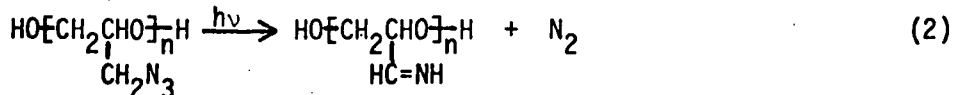
To reduce possible interferences from the presence of oxygen all samples were vacuum degassed, returned to atmospheric pressure with air, and sealed prior to irradiation. The only samples observed to undergo detectable color changes contained ferrocene as the catalyst. The faint greenish appearance was attributed to the formation of the ferrocenium ion (1). To determine if the air above the sample had an effect, samples were prepared by replacing the air with a pure nitrogen or oxygen atmosphere. Similar rates were obtained with both nitrogen and oxygen although they were slightly greater than obtained with air. As minimal effects were noted with the pure gases, air was used in conducting all other experiments.

Laser irradiation at 266 and 355 nm (Table II) was shown to have significant influence on the iron(III) acetylacetonate (FeAA) catalyzed reaction rates. To determine if this increased catalytic influence was common to other metal acetylacetonates, a series of these compounds was subjected to laser irradiation. Representative reaction viscosity data for the chromium(III), vanadyl(IV), and cobalt(III) acetylacetonates are shown in Table III and compared with the corresponding iron(III) compound. Little or no photoenhancement on the reaction rate was found with these additives and many other similar metal acetylacetonates. Table I shows additional metal acetylacetonates which were subjected to ultraviolet lamp irradiation and found to have little or no affect on these reactions.

A series of experiments was performed utilizing glycidyl azide prepolymer (GAP), which is an energetic azido containing polyol, to determine its stability in the presence of intense irradiation. It is known that the azido group absorbs strongly in the 266 nm region, and its compounds are highly susceptible to ultraviolet decomposition. Typically, alkyl azido decomposition occurs with the liberation of free nitrogen and the formation of imines as shown in reaction 1.

$$R_3CN_3 \xrightarrow{h\nu} R_2C=NR + N_2 \tag{1}$$

GAP was observed to undergo ultraviolet laser decomposition in accordance with reaction 2.

$$HO\text{-}(CH_2CHO)_n\text{-}H \xrightarrow{h\nu} HO\text{-}(CH_2CHO)_n\text{-}H + N_2 \tag{2}$$

$$\underset{CH_2N_3}{|} \qquad \underset{HC=NH}{|}$$

Copious amounts of nitrogen gas were produced and found entrapped in the gumstock during irradiation at both 266 nm, and to a lesser extent, at 355 nm. At 532 nm, laser irradiation for up to 1.5 hours did not result in any noticable decomposition of GAP. No significant photo-enhancement was observed to occur at 532 nm in the presence of FeAA.

Spectra for the six active organometallic catalysts selected for laser testing were obtained and molar extinction coefficients (Table IV) were calculated at 266, 355, and 532 nm.

DISCUSSION

The objective of these investigations was to examine the influence of monochromatic ultraviolet and visible radiation on isocyanate-polyol-organometallic catalyzed reactions to determine if reactive intermediates could be photoinduced which could affect the mechanism or rate of these reactions. Various mechanisms have been proposed for these reactions (2, 3).

The absorption of ultraviolet or visible light by a complex may cause one of three effects: (1) the rupture of a bond within the complex, (2) electron transfer between a ligand and the central metal atom, or (3) creation of an electronically excited complex. As previously mentioned, metal acetylacetonate complexes are reported to form charge transfer intermediates with isocyanates. It is proposed here that either the formation of the metal-isocyanate complex is facilitated or the complex itself is photoactivated by the laser towards attack by the OH group of the polyol. Although no detailed kinetic or mechanistic studies were undertaken during the course of this work, the results do agree with that of others in which an organometallic-isocyanate complex is postulated to be an intermediate in urethane formation.

The reactions of isocyanates with compounds containing active hydrogen are known to be profoundly influenced by catalytic additives (4). For example, it has been speculated that the reaction of an isocyanate with an alcohol in the presence of tetravalent tin catalysts occurs through the formation of an intermediate complex between the catalyst and the alcohol. The formation of a donor-acceptor bond between the oxygen of the alcohol and the tin of the catalyst activates the hydrogen on the hydroxyl group and increases the overall rate of reaction. In this situation, electro-philic attack by hydrogen on the isocyanate nitrogen could result in the formation of a strong hydrogen bond and the subsequent development of the covalent N-H bond.

Other investigators report the apparent formation of transition metal charge transfer complexes in polyol-isocyanate complexes (5). The absorption peaks are indicative of $d \longrightarrow d$ electronic transitions within a transition metal ion or of $\pi \longrightarrow \pi^*$ electronic transitions between the isocyanate and metal ion.

An examination of the summarized results in Table V give conclusive support for a laser-induced photoenhancement of metal catalyzed polyol-

isocyanate reactions. In five of the six samples selected for laser examination at the three wavelengths shown, it was found that the rate enhancements were both wavelength and catalyst dependent. The sixth sample (ferrocene) showed minimal photolytic activity. It is important to emphasize that two main requirements are needed to achieve photoenhancement in these reactions. These requirements are: (a) a catalytically active ingredient, such as an organometallic compound, and (b) photoactive species. It is apparent from the data (Table V) that no photoenhancement could be induced in the non-additive containing polyol-isocyanate reaction. Also, only a limited number of the many additives which are known to exert significant chemical catalysis were found to be additionally photochemically activated at the wavelengths examined. The variations in rate can also be seen to be wavelength dependent (Table V). This wavelength dependence can be attributed to the relative ability of the complex to enter into a photoactivated or excited state that is important in the rate determining step.

In the present system, it is reasonable to assume that the mechanism is very similar to that which is operative in the non-photoactivated reaction. The basis for this assumption is that the photoenhancement effects are of secondary importance when compared to the enhanced reaction rates obtained by chemical catalyst concentration changes. Laser photoactivation of the intermediate complex provides energy necessary to further enhance the catalyzed reaction.

The observation that only a limited number of the approximately sixty metal complexes tested resulted in enhanced photochemical reactions is attributed to the lack of activation of specific metal-ligand bonds. The positive results obtained with FeAA suggested that other acetylacetonate compounds might also produce similar effects. A series of acetylacetonates were evaluated with ultraviolet lamps and, in some instances, with the Nd:YAG laser. The data presented in Tables I and III show that photochemical activation was obtained only with iron(III) acetylacetonate. However, wavelengths other than those used in these investigations may result in photoactivation of metal additives which did not show any significant rate enhancement.

An interesting observation concerning the three ferrocene derivatives listed in Table V is apparent from the percent change in viscosities of the samples. The photorate enhancement increases are in direct relation to the increasing order of the electron withdrawing ability of the groups attached to the ferrocene ring. The order is as shown.

1,1'-Ferrocenedicarboxylic Acid > Benzoylferrocene > Ferrocene

CONCLUSIONS

These studies indicate significant enhancement of the polymerization rate of organometallic catalyzed polyol-isocyanate reactions can be

obtained with a Nd:YAG ultraviolet/visible laser. This enhancement is wavelength and catalyst dependent. While the precise mechanism is not known, the photorate enhancement appears to be dependent on the formation of an activated metal-isocyanate complex. With the exception of dibutyltin diacetate, the only additives which gave enhanced photochemical activity at 266, 355, and 532 nm were those organometallic compounds containing iron as the central metal atom. However, not all the iron compounds screened showed photoenhancement under the conditions of the experiments. These investigations indicate the laser can be used to enhance and control urethane formation reaction rates and opens the possibility that, through proper wavelength selection, other compounds may act as photocatalysts in these or other types of reactions.

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TABLE I

ORGANOMETALLIC COMPOUNDS SCREENED BY ULTRAVIOLET (UV) LAMPS

Compounds	Viscosity (poise)		
	Reference	254nm	366nm
Hexamminecobalt(III) Chloride	56	44	63
Cobalt Phthalocyanine	50	58	60
Bis(salicylidene)ethylenediamine Chromium(III)	57	62	60
Cobaltic Acetylacetonate	43	62	53
Cobaltocene	62	69	60
Cobalt Octoate (6%)	57	69	62
Manganic Acetylacetonate	88	71	67
Manganese Carbonyl	63	60	56
Manganous Acetylacetonate Hydrate	62	56	60
Nickel Dimethylglyoxime	60	63	61
Nickelocene	55	53	50
Bis(salicylidene)ethylenediamine Nickel(II)	54	55	56
Nickel Phthalocyanine	54	55	51
Titanium Oxyacetylacetonate	60	60	62
Bis(acetylacetanato)titanium Dichloride	60	65	63
Titanium Phthalocyanine	56	52	57
Zirconocene Dichloride	56	60	61
Chromic Acetylacetonate	55	52	54
Chromium Octoate (10.5%)	54	54	55
Bis(salicylidene)ethylenediamine Chromium(III)	54	54	50
Vanadyl(IV) Acetylacetonate	100	98	85
Barium Acetylacetonate Hydrate	52	53	63
Zinc Naphthenate (8%)	52	61	54
Cerium Acetylacetonate	54	54	56
Lead Phthalocyanine	54	53	52
Potassium Nitroprusside	57	60	52
2,3-Butanedione	45	52	52
Cupric Thiocyanate	51	52	52
Cupric Hexamethylenetetramine	49	52	50
Copper Stearate	52	53	51
Copper Phenylacetylide	80	82	78
Copper Biuret	52	55	54
Copper Phthalocyanine	52	51	54
Copper Naphthenate (8%)	86	78	73
Cupric Phenylacetate	104	102	102
Cupric Ferrocyanide	61	62	61
Copper(II) Ethylacetoacetate	113	109	100

TABLE I (continued)

Compounds	Viscosity (poise)		
	Reference	254nm	366nm
Cupric p-Toluenesulfinate	76	74	73
Copper Phenylacetylide	120	122	114
Copper 3-Phenylsalicylate	107	111	99
Cupric Dipivaloylmethane	93	106	83
Iron Naphthenate (6%)	84	82	89
Ferric Ammonium Citrate	63	62	71
*Ferric Cupferrate	78	137	140
Iron Octoate (6%)	78	83	97
Ferrous Gluconate	63	63	63
Iron Tristearate	65	63	65
*1,1'-Ferrocenedicarboxylic Acid	70	78	146
*Benzoylferrocene	88	107	122
Acetylferrocene	242	254	254
Ferrocenecarboxylic Acid	236	284	277
Bis(Hydroxymethyl)ferrocene	231	251	248
1-Ferrocenyl-1,3-butadiene	461	424	490
1,10-Phenanthroline Ferrous Sulfate (0.025M solution)	127	127	127
Iron Resinate	162	164	176
Ferric Potassium Oxalate	124	124	127
Ferric Ammonium Oxalate	138	130	133
Molybdenum Naphthenate	141	141	141
Cobalt Naphthenate	136	138	136
Cupric Naphthenate	156	159	156
*Ferrocene	98	132	122
*Dibutyltin Diacetate	217	283	221

*Selected for laser examination.

TABLE II

PGA/HMDI(IPDI) CATALYZED BY ORGANOMETALLIC COMPOUNDS

Wavelength (nm)	Time (hours)	Viscosity (poise)	
		Control	Irradiated
IRON(III) ACETYLACETONATE			
532	0.5	110	100
	1.0	178	153
	1.5	288	320
355	0.5	156	157
	1.0	299	479
	1.5	484	1021
266	0.5	122	153
	1.0	185	257
	1.5	427	808
DIBUTYLTIN DIACETATE			
532	0.5	116	104
	1.0	180	131
	1.5	261	261
355	0.5	81	81
	1.0	98	107
	1.5	123	130
266	0.5	114	115
	1.0	132	156
	1.5	275	413

TABLE II (continued)

FERROCENE

532	0.5	61	61
	1.0	63	61
	1.5	52	61
355	0.5	66	74
	1.0	69	78
	1.5	74	88
266	0.5	60	58
	1.0	60	65
	2.0	60	81

BENZOYLFERROCENE

532	0.5	75	81
	1.0	88	108
	1.5	95	144
	2.0	94	162
355	0.5	130	114
	1.0	–	239
	1.5	–	363
	2.0	283	438
266	0.5	46	52
	1.0	–	66
	1.5	–	89
	2.0	86	101

TABLE II (continued)

FERRIC CUPFERRATE

532	0.5	71	87
	1.0	,79	109
	1.5	81	120
	2.0	99	128
355	0.5	144	254
	1.0	-	352
	1.5	-	444
	2.0	208	583
266	0.5	55	61
	1.0	-	66
	1.5	-	84
	2.0	81	98

1,1'-FERROCENEDICARBOXYLIC
  ACID

532	0.5	72	87
	1.0	78	113
	1.5	76	134
	2.0	75	166
355	0.5	52	43
	1.0	-	69
	1.5	-	92
	2.0	55	138
266	0.5	40	43
	1.0	-	43
	1.5	-	·46
	2.0	55	55

TABLE III

EFFECTS OF METAL ACETYLACETONATES ON PGA/HMDI
REACTION AT 355 nm

Acetylacetonate	Time (Hours)	Viscosity (poise) Control	Irradiated
Chromium(III)	0.5	54	54
	1.0	55	53
	1.5	55	56
Vanadyl(IV)	0.5	65	62
	1.0	81	76
	1.5	91	83
Cobalt(III)	0.5	55	55
	1.0	55	56
	1.5	50	62
Iron(III)	0.5	156	157
	1.0	299	479
	1.5	484	1021

TABLE IV

MOLAR EXTINCTION COEFFICIENTS

COMPOUND	266 nm	355 nm	532 nm
Ferrocene	1.48×10^3	9.50	3.17
Benzoylferrocene	5.65×10^3	6.69×10^2	1.88×10^2
1,1'-Ferrocenedicarboxylic Acid	6.82×10^3	3.53×10^2	0.0
Ferric Acetylacetonate	1.90×10^4	2.58×10^3	3.30×10^2
Ferric Cupferrate	1.85×10^4	3.67×10^3	0.0
Dibutyltin Diacetate	6.42	0.0	0.0

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TABLE V

VISCOSITY CHANGES AT VARIOUS
WAVELENGTHS DUE TO PHOTOCATALYTIC ACTIVITY

Catalyst	Viscosity Change in poise 266	355	532
None	0 (0%)*	0 (0%)	0 (0%)
Ferrocene	21 (35%)	133 (19%)	9 (17%)
Benzoylferrocene	14.4 (17%)	155.8 (55%)	68 (72%)
1,1'-Ferrocenedicarboxylic acid	0 (0%)	83.5 (151%)	86 (121%)
Ferric Acetylacetonate	381 (89%)	537 (111%)	32 (11%)
Ferric Cupferrate	17.3 (21%)	375 (180%)	29 (29%)
Dibutyltin Diacetate	138 (50%)	6.9 (6%)	0 (0%)

(*)Percent viscosity change of the irradiated sample compared to the control.