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## Effect of Light on $\text{TiCl}_4$ -Induced Cationic Model Reactions

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### ABSTRACT

On exposure to UV or visible light,  $\text{TiCl}_4$  readily decomposes homolytically and yields  $\text{TiCl}_3$  plus chlorine. Similarly, irradiation of  $\text{TiCl}_4$ -hydrocarbon systems produce chlorinated hydrocarbon and HCl. 2,4,4-Trimethyl-1-pentene, a nonpolymerizable model for isobutylene, rapidly dimerizes in the presence of  $\text{TiCl}_4$  during irradiation with UV and visible light and yields a mixture of conventional head-to-tail  $\text{C}_{16}$ -olefins. While conversions are higher in the presence of light than in darkness, the structures of the dimers formed under these conditions are indistinguishable. The structures of these dimers of 2,4,4-trimethyl-1-pentene are incompatible with the cation-radical initiation mechanism of isobutylene polymerization effected by  $\text{TiCl}_4$  under irradiation proposed by Czechoslovak investigators. Polymerization by condensation experiments have been carried out in the dark and in visible light, and an interpretation of this

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phenomenon that complements the one proposed by French authors has been developed.

## INTRODUCTION

Titanium tetrachloride exhibits unique and unexpected properties as a coinitiator for cationic polymerizations. Cheradame et al. [1-3] reported that rapid polymerization to high molecular weight products ensued when quiescent mixtures of isobutylene- $\text{TiCl}_4$  or cyclopentadiene- $\text{TiCl}_4$  were distilled under high vacuum from one branch of an H-shaped glass vessel into the other. As polymerization occurred upon condensation, the authors termed this phenomenon "polymerization by condensation." Sigwalt et al. [4, 5] found that  $\text{TiCl}_4$  can induce polymerization of  $\alpha$ -methylstyrene and dimerization of 1,1-diphenylethylene in the absence of protogen at monomer/ $\text{TiCl}_4$  ratios lower than 100. A generally accepted explanation for these surprising observations has not yet been proposed.

Marek et al. [6-8] reported that  $\text{TiCl}_4$  and  $\text{VCl}_4$  initiate the polymerization of isobutylene in the presence of visible light, i. e., a conventional 60 W tungsten bulb. The molecular weights of the polymers produced in this manner were exceptionally high, even at relatively high temperatures e. g.,  $-40^\circ\text{C}$ . Initiation was proposed to occur by cation radicals arising via charge-transfer complexes between a  $\text{TiCl}_4$  acceptor and an isobutylene donor, i. e., by electron transfer from the olefin to the Lewis acid. The formation of high molecular weight product was explained by assuming that the cation radicals rapidly combine to dications which can grow from both ends.

Recently, we found [9] that glow discharge and UV light in the presence of  $\text{TiCl}_4$  readily induce polymerization of isobutylene. Highly purified  $\text{TiCl}_4$ , when exposed to daylight for several hours or to ordinary diffuse laboratory light for several days in sealed glass (Pyrex) tubes, starts to decompose, and a fine brown precipitate ( $\text{TiCl}_3$ ) settles out. Similarly, purest  $\text{TiCl}_4$ -methylene chloride solutions, when exposed to daylight for several hours in glass tubes, turn yellow and deposit a brown-violet precipitate of  $\text{TiCl}_3$ .

These key observations and the above-mentioned phenomena described by French and Czechoslovak authors, prompted us to investigate in some detail the photochemical behavior of  $\text{TiCl}_4$  and its solutions in the presence of different sources of light. We also examined the properties of  $\text{TiCl}_4$  solutions under simulated cationic polymerization conditions using 2,4,4-trimethyl-1-pentene as a nonpolymerizable model compound for isobutylene. These studies provide improved insight into the understanding of polymerizations involving  $\text{TiCl}_4$  and similar transition metal halides.

## EXPERIMENTAL

Materials and Their Purification

TiCl<sub>4</sub> (Ventron Co., 99.9%) was distilled once in a nitrogen atmosphere and twice in a high vacuum from 1.5% sodium amalgam and stored over sodium mirror in vacuo at ca. -40°C in the dark. Prior to the experiment TiCl<sub>4</sub> was further purified by passing the vapor over a liquid potassium-sodium alloy (83% K) and condensing it into the pipet side-arm of the reactor (Fig. 1).

Isobutylene (Union Carbide Co., 99.0%) was purified by passing the gas first through a column filled with molecular sieves (Union Carbide Co., 3Å) and subsequently through two steel cylinders filled with liquid K-Na alloy at 140°C (first cylinder) and 240°C (second cylinder). The apparatus for purification of isobutylene is shown in Fig. 2. The desired amount of isobutylene was condensed over a fresh sodium mirror and stored under pressure in a glass ampoule at ~0°C. The amount of isobutylene was determined from the flow rate (usually 40-50 ml/min).

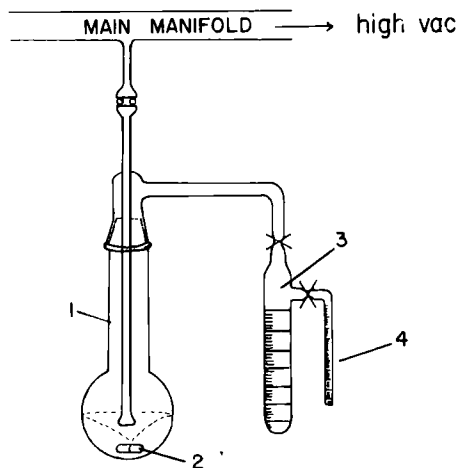


FIG. 1. Apparatus for purification of TiCl<sub>4</sub> with liquid sodium-potassium alloy and reactor for polymerization of isobutylene: (1) reservoir with K-Na (83:17 by weight) alloy; (2) magnetic stirring bar; (3) reactor; (4) 0.2/0.01 ml pipet to measure TiCl<sub>4</sub>; (x) constructions for sealing.

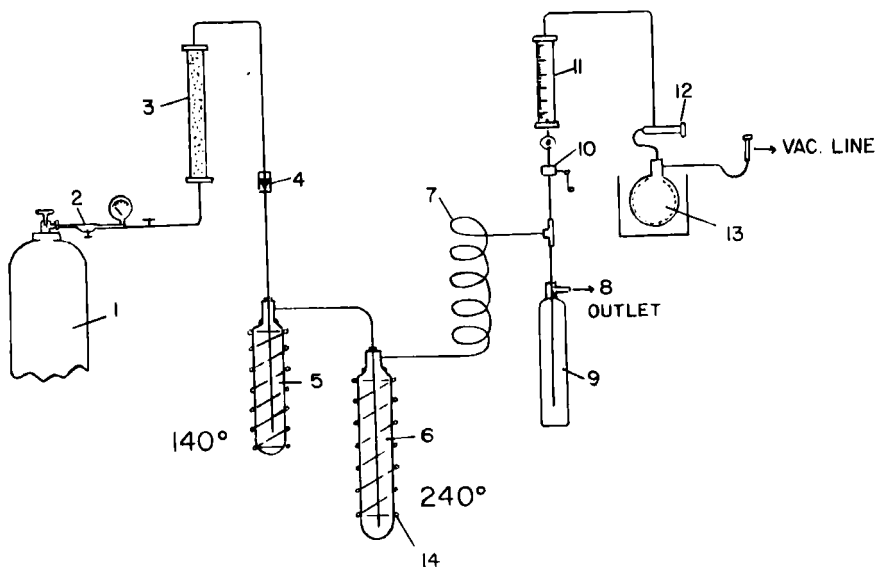


FIG. 2. Scheme of apparatus used to purify isobutylene: (1) isobutylene cylinder; (2) regulator with manometer ( $p = \text{const} = 1.38 \text{ atm}$ ); (3) column with 4 Å molecular sieve pellets ( $h = 35 \text{ cm}$ ); (4) one-way valve; (5, 6) steel cylinders filled with Na-K alloy ( $h = 32 \text{ cm}$ ) heated to  $140^\circ\text{C}$  (5) and ( $h = 44 \text{ cm}$ ) and  $240^\circ\text{C}$  (6); (7) stainless steel cooling coil ( $1/4 \text{ in.}$ ); (8) check valve ( $15 \text{ atm}$ ); (9) empty steel cylinder; (10) cut-flow valve; (11) flowmeter with regulating valve (to  $100 \text{ ml/min}$ ); (12) Hi vac valves; (13) flask for condensation of pure isobutylene with shiny sodium mirror; (14) heating mantle.

This purification procedure has also been used in experiments described earlier [9].

Hexane (Mallinckrodt Co., A. P., a mixture of *n*-hexane and other isomers, mainly methylcyclopentane) was refluxed with fuming sulfuric acid, washed with aqueous NaOH, then with distilled water, dried with  $\text{CaH}_2$  and distilled twice over  $\text{CaH}_2$  in a nitrogen atmosphere. Subsequently the solvent was distilled from a sodium dispersion ( $50 \mu$ ) into the vacuum line by using the apparatus shown in Fig. 3 (reflux 1:25). Final distillations were made from a shiny sodium mirror under high vacuum.

Methylene chloride (Fisher Scientific Co. R. G.) was stirred for several days under high vacuum with a sodium dispersion, and distilled twice over a shiny sodium mirror under high vacuum.

2,4,4-Trimethyl-1-pentene (TMP) (Chemical Samples Co., 99.9%)

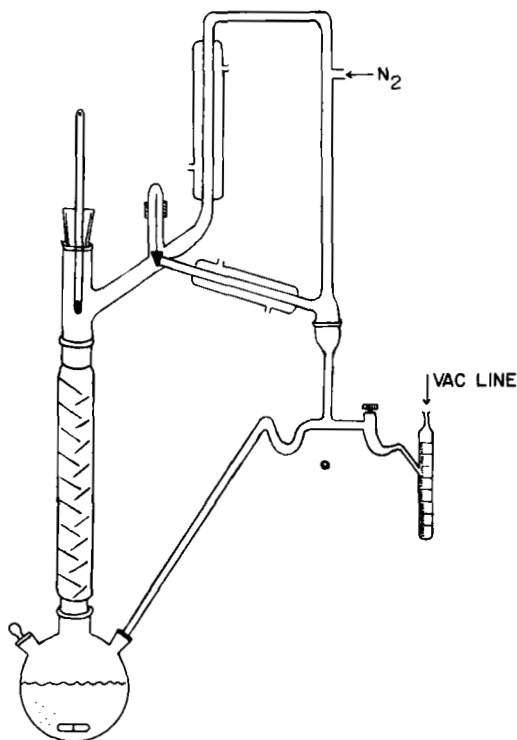


FIG. 3. Apparatus for continuous distillation of solvents with connection to high vacuum line.

was distilled over CaH<sub>2</sub> in a nitrogen atmosphere (101-101.5°C fraction) and twice over a sodium dispersion and finally twice over a shiny sodium mirror under high vacuum.

### Techniques

All operations were carried out in semi-darkness, with lights turned off in a windowless room. Faint, diffuse light was admitted only through a door from an adjacent room. The main manifold and flasks of the high vacuum line were covered with aluminum foil. In a typical experiment, hexane or methylene chloride was distilled into a graduated 7740 Pyrex (transmittance < 30% for 300 nm) reactor. Then TiCl<sub>4</sub> was introduced by distilling it first into a

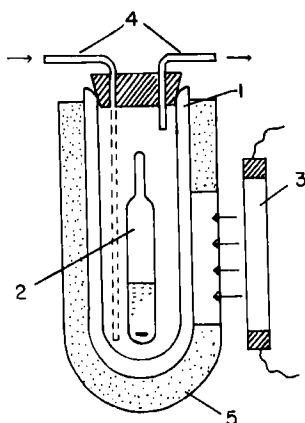


FIG. 4. Equipment for irradiation: (1) evacuated quartz jacket; (2) quartz (or Pyrex) reactor with stirring bar; (3) light source (UV lamp, or tungsten bulb); (4) inlet and outlet of circulating coolant; (5) insulation.

disposable pipet 0.01/0.5 ml (Fig. 1), and then into the reactor. The volume of  $\text{TiCl}_4$  transferred into the reactor was determined from the graduations on the pipette which was then sealed off.

TMP was distilled into the reactor at liquid nitrogen temperature, sealed off and placed into a quartz Dewar flask filled with a circulating coolant maintained at constant temperature ( $\pm 0.5^\circ\text{C}$ ). (Fig. 4). Reaction mixtures were irradiated by a 450-W medium-pressure mercury lamp (Hanovia 450 W), a General Electric EBW-82 daylight bulb, or a 60-W Sylvania tungsten bulb. The distance from the light source to the reactor was 10 cm. Experiments summarized in Table 1 were made as follows. In the apparatus shown in Fig. 5,  $\text{TiCl}_4$ , purified as shown in Fig. 1, was distilled into pipet P and a desired amount into chamber I. Subsequently, pipet P was removed, methylene chloride was distilled into chamber I, and the solution was kept at  $-52^\circ\text{C}$  while isobutylene was distilled into it. The reactor was sealed off at X and the mixture was stirred for 30 min at  $-52^\circ\text{C}$  and then heated to ca.  $10^\circ\text{C}$ . Chamber II was rinsed with the reaction mixture. Chamber I was cooled to  $-52^\circ\text{C}$  for 30 min, and its content was distilled rapidly into chamber II cooled with liquid nitrogen. After distillation was complete (ca. 2.5 min), chambers I and II immediately were separated and ca. 3 ml methanol was introduced into each chamber. The polymers were isolated, dissolved in hexane and dried to constant weight in vacuo.

The curves shown in Fig. 6 were obtained as follows.  $\text{TiCl}_4$  and

TABLE 1. Polymerization of Isobutylene with TiCl<sub>4</sub>-Methylene Chloride Solution with Simultaneous Condensation: Comparison of Various Polymerization by Condensation Experiments

Conditions	Temp, °C	Isobutylene (M)	TiCl <sub>4</sub> (M)	Yield (%)		Ref		
				Prepolymerization	Polymerization by condensation (temp. of liq. N <sub>2</sub> )			
Darkness	-53 <sup>a</sup>	1	0.74	1.57	18.5	10.7	29.2	This
Light <sup>a</sup>	-52	0.68	0.68	1.51	24.5	56.7	81.2	work
Semidarkness	-70	0.5	0.5	1.5	6.0	77 <sup>b</sup>	83	[2]
Light	-72	0.74	0.74	1.0	36	64 <sup>b</sup>	100	
Light	-50	0.603	0.603	1.6	16.5	83.5	100	[3]
Light	-50	6.23	6.23	1.55	30	63.2	93.2	

<sup>a</sup>Average of two experiments.

<sup>b</sup>Condensation at -78°C.



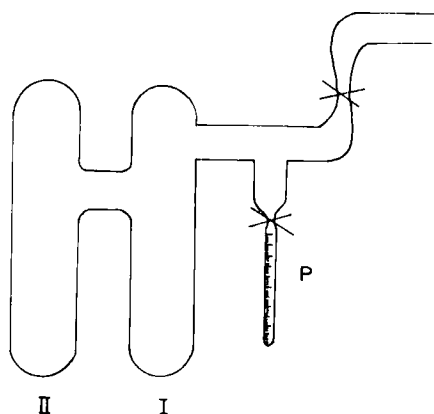


FIG. 5. Apparatus for polymerization by condensation experiments.

hexane or methylene chloride were distilled into the Pyrex tube under high vacuum and irradiated by a 450-W Hanovia lamp. The volatiles were distilled off, and a brown deposit ( $\text{TiCl}_3$ ) remained on the walls of the tube. The tubes were sealed and weighed. Then they were cut open, washed with successively 10% sulfuric acid and distilled water, and weighed again to determine the amount of  $\text{TiCl}_3$ .

### Analysis of Products

Liquids were analyzed by using a Hewlett-Packard 5750 gas chromatograph with a flame detector; conditions: high efficiency SE-30 (12 ft  $\times$  1/8 in.), helium carrier gas at 270°C, 8°C/min temperature rise in the range 70-270°C.

Molecular weights were determined by using a Chromalitics MC-2 mass chromatograph, with  $\text{SF}_6$  and  $\text{CO}_2$  carrier gases, in the temperature range 70-275°C.

NMR spectra of single components and reaction mixtures were obtained with a Varian HR 300 MHz spectrometer by using  $\text{CCl}_4$  solutions with TMS internal standard.

IR spectra were obtained with a Perkin-Elmer 521 grating spectrometer with a 0.5 mm liquid cell (without reference cell).

Molecular weights of polymers were determined by using a Waters Associates high-pressure liquid chromatograph with five microstyrogel columns and THF as carrier solvent.

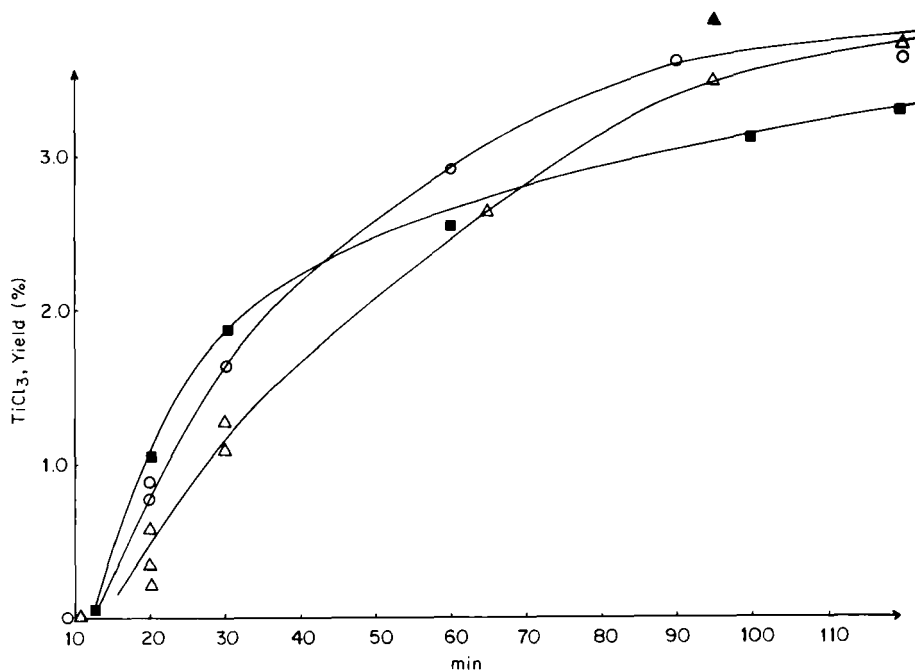


FIG. 6. The effect of illumination time on TiCl<sub>3</sub> formation: (○) 1.35 M TiCl<sub>4</sub> in methylene chloride; (△) 1.32 M TiCl<sub>4</sub> in hexane; (▲) after 60 min irradiation lamp was rotated 180° around the reactor; (■) 1.31 M TiCl<sub>4</sub> in TMP; Pyrex tube, 450-W Hanovia lamp, -20°C.

## RESULTS AND DISCUSSION

### Observations with Neat TiCl<sub>4</sub>

Highly purified TiCl<sub>4</sub> (prepared in the dark), when exposed to daylight by placing it in sealed Pyrex tubes in a window, starts to decompose within hours to form a fine dark brown precipitate, mostly TiCl<sub>3</sub>. In contrast, TiCl<sub>4</sub> in Pyrex tubes protected from light by an aluminum wrap remains unchanged.

After flask-to-flask distillation of TiCl<sub>4</sub> in the high vacuum assembly, many small brown spots and iridescence were observed to form in the manifold connecting the TiCl<sub>4</sub> source-flask and receiver. It was determined that the brown deposit is mainly TiCl<sub>3</sub> and that

iridescence may be due to finely dispersed  $\text{TiCl}_3$  on the surface of this glass.

To explain these observations, it is postulated that  $\text{TiCl}_4$  may photolyze to  $\text{TiCl}_3$  plus chlorine, even under relatively mild conditions:



The low photolytic stability of  $\text{TiCl}_4$  under UV or visible light is not too surprising, considering that the Ti-Cl bond is one of the weakest chemical bonds known with a bond energy of  $26 \pm 2$  kcal/mole [ 10]. Experiments and observations that corroborate this postulate are described in the following sections.

### Observations with $\text{TiCl}_4$ Solutions

As with neat  $\text{TiCl}_4$ , a brown precipitate was observed to form after several days of exposure to daylight of hexane or methylene chloride solutions of  $\text{TiCl}_4$  in sealed Pyrex tubes. A control tube protected from light remained colorless, unchanged for months.

In a series of experiments,  $\text{TiCl}_4$ -hexane and  $\text{TiCl}_4$ -methylene chloride solutions in Pyrex tubes were illuminated by UV light and the rate of  $\text{TiCl}_3$  formation was determined. Figure 6 shows the results. These experiments were carried out in individual glass (Pyrex) reactors, and the amount of the dark brown coatings on the walls was determined gravimetrically. That the brown deposit is mainly  $\text{TiCl}_3$  was established by analysis of their sulfuric acid solutions. The brown color of the deposit may also indicate the presence of  $\text{TiCl}_2$ . Irradiation intensity diminished due to the accumulation of  $\text{TiCl}_3$  on the glass so that only the initial rates of  $\text{TiCl}_3$  formation may be of kinetic significance. The rate of  $\text{TiCl}_4$  decomposition is relatively high in both solvents but it may be higher in the polar medium.

In this context it is of interest that Puxeddu mentioned almost a half century ago that ether solutions of  $\text{TiCl}_4$  change color when exposed to sunlight [ 11]. Also, Bown and Lampe [ 12] claimed that  $\text{TiCl}_4$  vapor in the presence of Hg-vapors and UV light is reduced to  $\text{TiCl}_3$ . Beyond these and the aforementioned references, there is a dearth of information concerning photochemical properties of  $\text{TiCl}_4$  or its solutions.

Remarks on Polymerization by Condensation

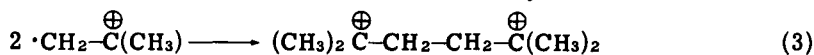
Our finding that TiCl<sub>4</sub> decomposes even under diffuse laboratory light may contribute to the understanding of the phenomenon of polymerization by condensation. We theorize that polymerization by condensation occurs because, during distillation of isobutylene-TiCl<sub>4</sub> mixtures, TiCl<sub>4</sub> may decompose by photolysis to TiCl<sub>3</sub> + Cl· and that the latter in the presence of C-H bonds may yield HCl [9]; the HCl would provide the proton necessary in conjunction with TiCl<sub>4</sub> for efficient initiation of olefin polymerization. As it is well known, traces of protogenic substances e. g., HCl, H<sub>2</sub>O, suffice to induce rapid and efficient polymerization under such conditions [13, 14]. Although Cheradame et al. [2] mention an experiment carried out in the absence of light, this was not performed by wrapping the vacuum assembly by aluminum foil or a similar precaution to protect it from light but by turning off the light and working in a dimmed room [15].

We have carried out a set of polymerization by condensation experiments by using first a vacuum line carefully protected from light by wrapping it with aluminum foil and subsequently one exposed to illumination by a daylight bulb. Table 1 shows the data. Pre-polymerization yields, i. e., the yields obtained in chamber I of the assembly shown in Fig. 5, were within what is considered to be experimental variation, i. e., 18.5 and 24.5%, in darkness and light, respectively. In contrast, the second part of the experiment, which involves the distillation of the isobutylene-TiCl<sub>4</sub>-methylene chloride system from chamber I to chamber II, i. e., the actual polymerization by condensation step, gave a significantly higher yield in light (56.7%) than in darkness (10.7%).

These experiments prove that illumination by visible light of olefin-TiCl<sub>4</sub> mixtures in the vapor phase can cause initiation; however, one cannot state with finality that polymerization by condensation takes place only in the presence of light. This is in agreement with the results of French workers [2, 3] whose data are also presented in Table 1.

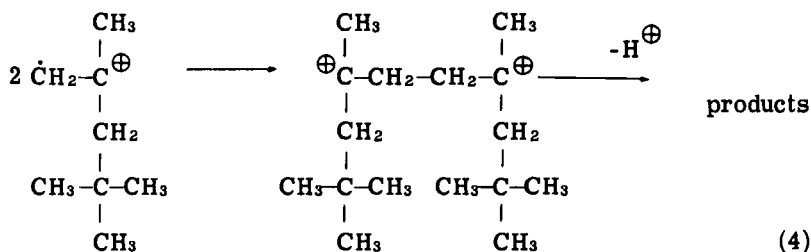
Model Experiments with 2,4,4-Trimethyl-1-pentene

This phase of our investigations concerns details of the initiation mechanism of light-induced polymerization of isobutylene in the presence of TiCl<sub>4</sub>, described by Czechoslovak workers [6-8]. According to these authors, initiation occurs via isobutylene cation-radicals which combine tail-to-tail to diisobutylene dication:



The isobutylene cation radicals have been detected by ESR spectroscopy; however, their recombination mechanism and their further decay is a matter of conjecture, and direct proof for these reactions has not been provided.

We decided to reinvestigate chemical consequences of these claims by the use of 2,4,4-trimethyl-1-pentene (TMP), a nonpolymerizable model of isobutylene. We planned to repeat the experiment of Marek et al. with this highly branched olefin and hoped to isolate products (most likely diolefins), arising from the tail-to-tail dimer dication [Eq. (4)].



We commenced our experiments by illuminating TMP-TiCl<sub>4</sub> mixtures with UV light. Similarly to observations made in the presence of hexane solvent, rapid TiCl<sub>4</sub> decomposition to TiCl<sub>3</sub> occurred as indicated by the appearance of dark brown precipitate. Figure 6 shows the results of a series of experiments in which 1.31 M TiCl<sub>4</sub> in TMP solutions were illuminated by a Hanovia lamp (450 W, λ > 280 nm) at -20°C. Evidently the initial rate of TiCl<sub>4</sub> decomposition is increased in the presence of olefin relative to systems containing hexane and methylene chloride. We speculate that the photolytic cleavage of Ti-Cl bonds is facilitated by the formation of olefin - TiCl<sub>4</sub> charge-transfer (CT) complexes. Isobutylene - TiCl<sub>4</sub> CT complexes have been shown to exist by Marek [8].

ESR spectroscopy of TMP-TiCl<sub>4</sub>-hexane mixtures at -196°C showed signals at ≈ 1.95 G which were broader than that reported by Marek [7]. We assign these signals, which developed during continuous irradiation with UV light, to TiCl<sub>3</sub>. We did not find evidence by ESR for the presence of organic radicals which may be due to our less than optimum radiation conditions in the cavity of the ESR instrument.

The products formed upon irradiation of TMP-TiCl<sub>4</sub>-hexane mixtures were analyzed by gas and mass chromatography, and NMR and IR spectroscopy. Pertinent data are summarized in Table 2 and Fig. 7. As shown by the results in Table 2, TMP-TiCl<sub>4</sub> systems, upon irradiation, yield a large quantity of dimers together with minor

TABLE 2. Yields of Chlorinated Compounds of TMP Obtained upon UV Irradiation<sup>a</sup>

Conditions	TMP (%)	Monochlorinated TMP (%)	Dichlorinated TMP (%)	Trichlorinated TMP (%)	Dimer of TMP (%)	Chlorinated TMP dimer and other unidentified products (%) <sup>b</sup>
TiCl <sub>4</sub>						
TMP = 5.04 M	10.2	Traces	≈ 2.3	8.6	76.2	2.4
TiCl <sub>4</sub> /TMP = 0.66						
VCl <sub>4</sub>						
TMP = 4.54 M	10.8	5.0	9.2	14.2	56.6	4.1
VCl <sub>4</sub> /TMP = 0.67						
Cl <sub>2</sub>						
TMP = 6.41 M	65.8	0.9	13.2	10.8	2.6	6.6
Cl <sub>2</sub> /TMP = 0.61						

<sup>a</sup>Irradiation: 30 min, Hanovia lamp, -70°C.<sup>b</sup>The relative composition of chlorinated and unidentified products is variable.

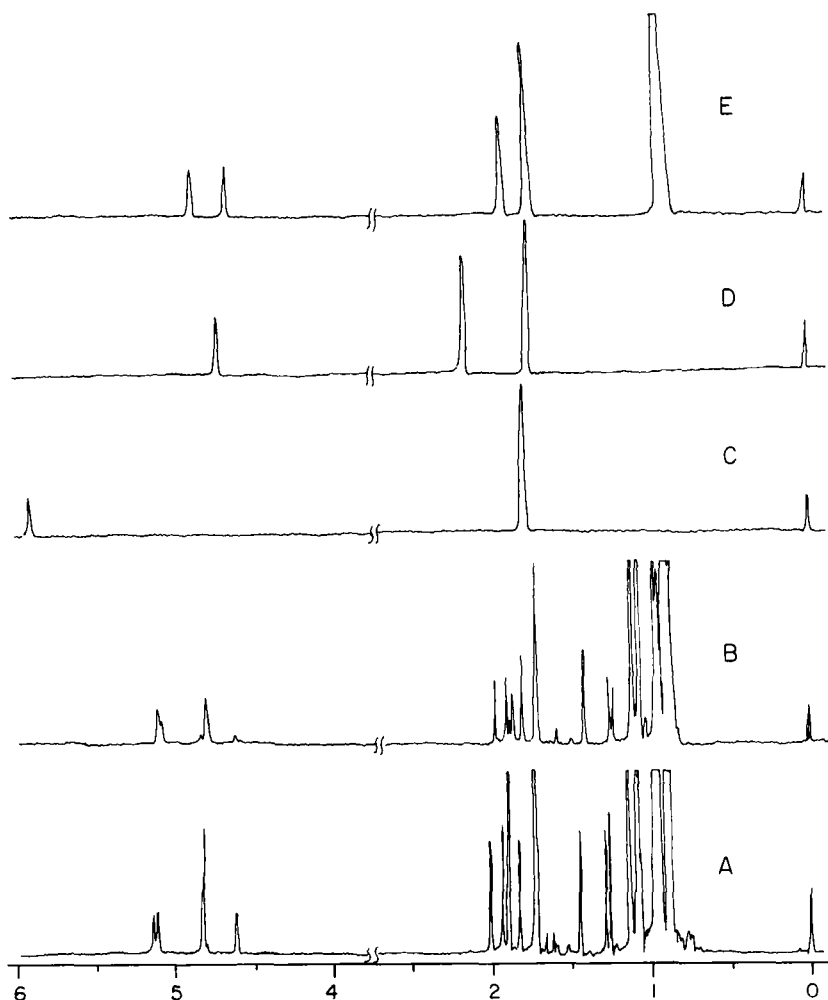
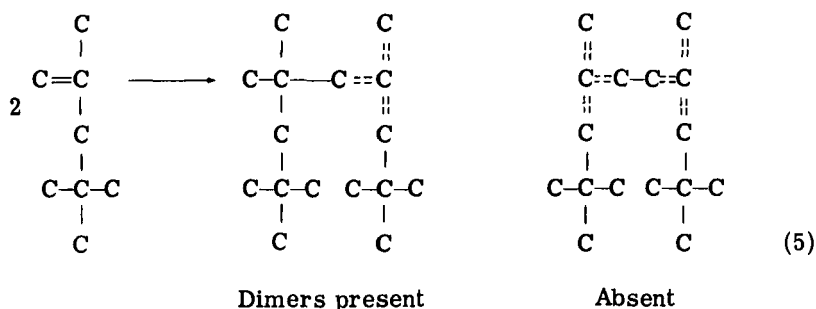


FIG. 7. NMR spectra of TMP/TiCl<sub>4</sub> mixtures (B) irradiated with UV light and (A) kept in darkness at -78°C; (C) 2,5-dimethyl-2,4-hexadiene; (D) 2,5-dimethyl-1,5-hexadiene; (E) TMP.

amounts of mono-, di-, and trichlorinated products. According to gas chromatography, using authentic compounds for comparison, three isomers of C<sub>16</sub>-olefins have been found. The exact position of the unsaturation could not be ascertained, however absence of this information does not diminish the trust of the argument.

Figure 7 shows key parts of NMR spectra of TMP-TiCl<sub>4</sub> mixtures exposed to UV irradiation and stored in darkness. The differences between the spectra obtained with the TMP-TiCl<sub>4</sub> system that was irradiated and that protected from light are negligible. Both spectra show resonances at  $\delta = 1.12$  and 1.16 ppm characteristic of protons in geminal methyl groups that exist in conventional head-to-tail C<sub>16</sub>-olefin isomers having external and/or internal double bonds. Resonances corresponding to conjugated internal double bonds, which would be present in the most favored tail-to-tail isomer (1,4-dimethyl-1,4-neopentyl-1,3-butadiene) arising by combination of TMP radical-cations, were absent. Similarly, IR spectra of irradiated and non-irradiated TMP/TiCl<sub>4</sub> mixtures were undistinguishable in the 700-800 cm<sup>-1</sup> region.

These data lead us to conclude that TMP in the presence of TiCl<sub>4</sub> in darkness or in UV light dimerizes to conventional head-to-tail olefins whose structures are quite similar if not identical [ Eq. (5)].



(The dotted lines indicate possible positions of unsaturations in the dimers.)

Data very similar to these were obtained by using VCl<sub>4</sub> instead of TiCl<sub>4</sub> and are shown in Table 2. However, the purity level of VCl<sub>4</sub> was not as high as that of TiCl<sub>4</sub>.

The structure of the products obtained in these experiments contain important information relative to the mechanism of the reactions involved. In line with our proposition above, that hydrocarbon TiCl<sub>4</sub> systems upon illumination yield HCl and consequently HCl-TiCl<sub>4</sub>, i. e., most efficient cationic initiating systems, we believe that the dimerization of TMP commences by protonation via the H<sup>+</sup>TiCl<sub>5</sub><sup>-</sup> hypothetical acid and progresses by conventional head-to-tail olefin addition to yield the C<sub>16</sub>-cation which is unable to sustain further propagation due to steric compression and rapidly loses proton (chain transfer).

The minor amounts of mono-, di-, and trichlorinated products found may arise by a variety of routes, e. g., initiation by Cl<sup>+</sup>/TiCl<sub>5</sub><sup>-</sup>,



TABLE 3. TMP Dimer Yield Obtained with Various Light Sources (30 min at  $-78^{\circ}\text{C}$ )

Light source	Initiator (M)		TMP (M)	Yield of TMP dimer (%)
	TiCl <sub>4</sub>	VCl <sub>4</sub>		
None	3.86	-	3.84	65.2
(darkness)	-	3.91	3.90	48.3
60-W Sylvania tungsten bulb	3.85	-	3.85	72.2
Daylight G. E. FBW-N.B.2 bulb	3.86	-	3.85	68.8
450-W Hanovia	3.85	-	3.85	83.4
(medium-pressure)	3.86	-	3.84	75.5 <sup>a</sup>
UV-Hg lamp	-	3.90	3.91	59.4

<sup>a</sup>TiCl<sub>4</sub> irradiated for 30 min prior to mixing with TMP; the TMP/TiCl<sub>4</sub> mixture was stored in darkness for 30 min at  $-78^{\circ}\text{C}$ .

hydrochlorination of TMP, chlorination of TMP, a combination of these.

Independent experiments in which TMP was chlorinated by Cl<sub>2</sub> in the absence of Lewis acid gave only an insignificant amount of C<sub>16</sub>-olefins, however, yielded relatively important quantities of the chlorinated products. The structure of the latter and those formed in experiments carried out in the presence of TiCl<sub>4</sub> and/or VCl<sub>4</sub> were largely identical. Some of this information is shown in the last line of Table 2.

Chlorine formed in the presence of light during TiCl<sub>4</sub> decomposition can attack olefin and alkane solvent. Indeed, we found that during UV irradiation of the most concentrated (4.52 M), TiCl<sub>4</sub> solution (hexane, 30 min) 2.3% unidentified chlorinated hexanes were formed.

In the course of these experiments it was observed that TMP-TiCl<sub>4</sub> and TMP-VCl<sub>4</sub> mixtures yield C<sub>16</sub>-olefins even in darkness. Extended series of experiments were carried out under a variety of conditions and the results together with pertinent information in regard to experimental conditions are shown in Table 3 and Figs. 8 and 9. The fact that a large amount of C<sub>16</sub>-olefin formed even in the

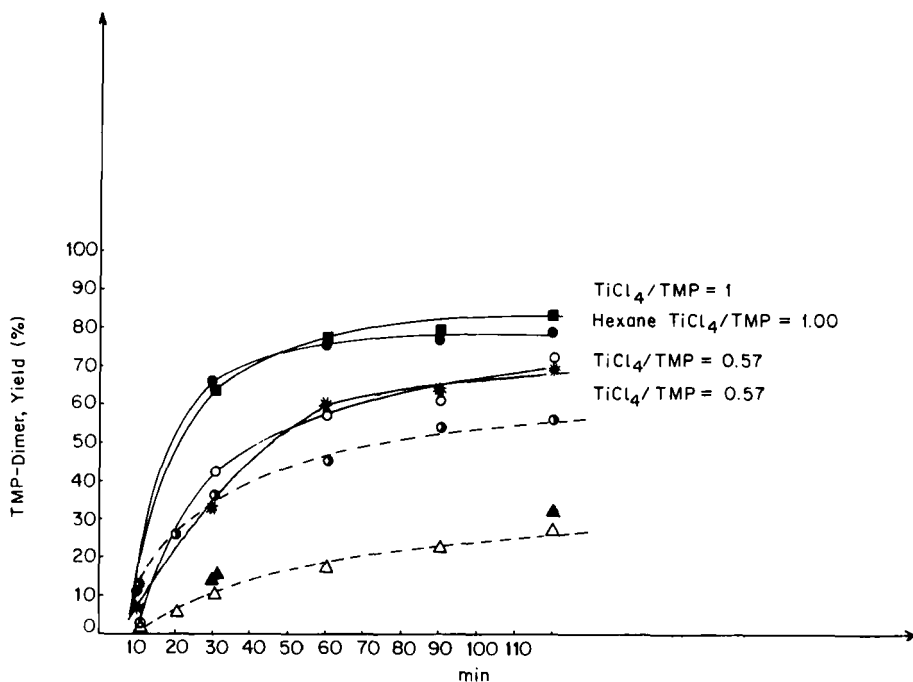


FIG. 8. TMP conversion vs. time in the dark at  $-78^{\circ}\text{C}$  at various  $\text{TiCl}_4/\text{TMP}$  ratios.  $\text{TiCl}_4/\text{TMP}$  ratios are indicated besides the curves. The dotted line indicates experiments in which TMP and  $\text{TiCl}_4$  were purified by treatment with K-Na alloy. In three experiments ( $\blacktriangle$ ) TMP was not purified by K-Na treatment.

dark is not too surprising, considering the mechanism of dimerization of TMP. Traces of unscavengeable protogenic impurities may start the chain which is being regenerated by the proton expelled after each dimerization step. Since termination is probably slow or absent because of the low amounts of impurities present, high conversions are attained. Illumination by shorter wave lengths increases  $\text{C}_{16}$ -olefin yield, however, the effect is small since it is obscured by high "control" values, i. e., yields obtained in darkness (Table 3). In an experiment in which the  $\text{TiCl}_4$  was preirradiated, i. e., irradiated prior to introducing TMP, the yield was 75.5%  $\text{C}_{16}$ -olefin.

At this point, considerable time and effort was spent to reduce the extent of dimerization of TMP by most exhaustive drying and

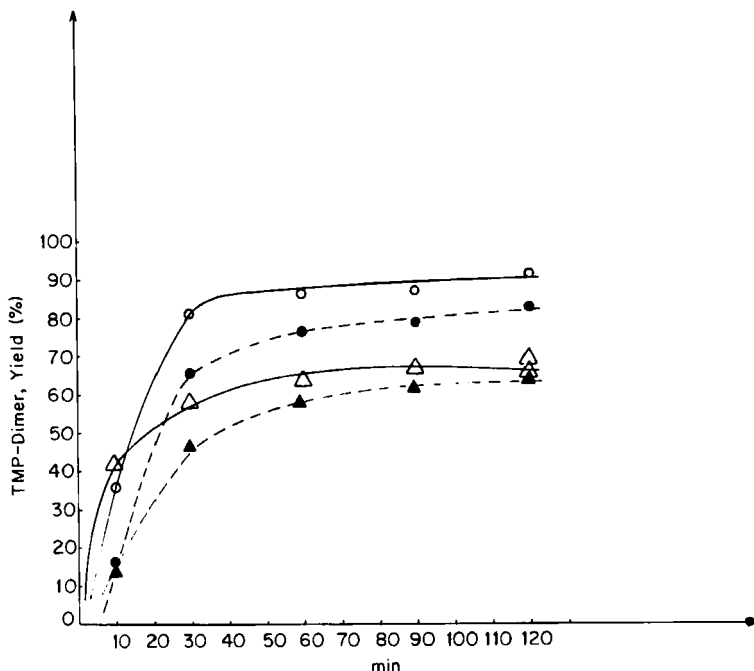


FIG. 9. Yield of TMP dimer vs. time obtained in presence of  $\text{TiCl}_4$  and  $\text{VCl}_4$  in the dark and with UV light at  $-78^\circ\text{C}$  at  $\text{TiCl}_4/\text{TMP} = 1$ : (●) dark and (○) irradiation;  $\text{VCl}_4/\text{TMP} = 1$ : (▲) dark and (△) irradiation.

purification of the apparatus and reagents used. Thus in a series of experiments the  $\text{TiCl}_4$  and TMP were distilled over liquid Na-K alloy; however, even under these conditions significant dimerization occurred (~55% at  $-78^\circ\text{C}$  and ~25% at  $-40^\circ\text{C}$  after 120 min). Evidently, it is impossible to scavenge completely all protogenic substances and/or chlorine from  $\text{TiCl}_4$  by this or similar techniques. Additional purification of solvent and TMP did not change the yield of the dimer (Fig. 8).

Our results are similar to those obtained by French workers [4, 5] for the dimerization of 1,1-diphenylethylene with  $\text{TiCl}_4$  in methylene chloride. The authors found that dimerization takes place without the addition of any protogenic promoter and results in the formation of a head-to-tail dimer of 1,1-diphenylethylene. Formation of an active olefin- $\text{TiCl}_4$  complex was proposed to explain this

phenomenon. The manner the charge transfer complex that is formed between the olefin and TiCl<sub>4</sub> [8] is transformed may depend on the wavelength of the light used for irradiation. Irradiation by visible light, e. g., 400-480 nm used by Marek et al. [6-8] may produce ion radicals, whereas the 280-540 nm light used in our experiments that produces Cl<sup>•</sup> will in turn lead to HCl and thus to a conventional Brønsted acid-Lewis acid initiator system.

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