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IDENTIFICATION AND QUANTIFICATION OF BY-PRODUCTS AND  
INTERMEDIATES IN THE PHOTOCATALYTIC OXIDATION OF GAS-PHASE  
TRICHLOROETHYLENE

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ABSTRACT

The results of a study of the photocatalytic oxidation of trichloroethylene (TCE) in air using titanium dioxide as the catalyst are reported. Dichloroacetyl chloride is found to be an intermediate in the oxidation sequence and carbon monoxide, phosgene, carbon dioxide, hydrogen chloride, and chlorine are found in the product mixture. The yields of each, except chlorine, have been determined using online Fourier transform infrared (FTIR) spectroscopy. Mass balances on both carbon and chlorine have been determined.

KEY WORDS

Photocatalysis, Trichloroethylene, Intermediates

1. INTRODUCTION

Photocatalytic oxidation of a gas phase over irradiated titanium dioxide is an effective method for the destruction of some classes of hazardous organic compounds. Following the report of Dibble and Raupp [1] that trichloroethylene (TCE) could be completely mineralized there have been other reports of studies of the destruction of organic compounds by this method [2,3,4,5,6]. Earlier work on the photocatalysed partial oxidation of hydrocarbons has been well documented [7,8]. Authors have reported that by-products of TCE destruction were not detected or were found only in trace amounts [1,2,3]. In contrast to these reports, we have found that some by-products are formed in significant yields. We report here

the **results** of a quantitative study of the mass balances on carbon- and **chlorine-containing** products for the photocatalytic oxidation of **TCE** under a variety of conditions.

## 2. EXPERIMENTAL SECTION

A diagram of the experimental apparatus is shown in Figure 1. The **flow** of feed gas to experimental apparatus is maintained by the injector assembly. It consists of two four-liter stainless steel **sample** cylinders. Liquid chemicals, such as TCE and water, are injected into these cylinders through heated syringe ports, then the cylinders are backfilled to a pressure between 80 and 160 psig with "zero grade air." The injector assembly may also **be** configured with syringe pumps for continuous operation. One delivery line from the assembly leads directly to the Fourier transform infrared (**FTIR**) spectroscopy for quantification of the mixtures. The second line is equipped with a two-stage regulator that provides a constant upstream pressure to a Matheson no. 604 rotameter which provides a quantitative flow rate through the system.

Downstream from the rotameter is a MKS Type 248B electronic control valve. This valve, along with a Type 116A controller, provides a signal to a Type 107A six-decade capacitance manometer mounted on the outlet of the **FTIR** cell. The control valve is directly upstream of a Vianon Model 218 pressure transducer. This is calibrated from 0-20 psia.

**Photoreactors** incorporate a fixed catalyst and annular flow regions. Each reactor consists of a glass tube coated on the inner surface with the anatase form of titanium dioxide. Inside the reactor tube is a fluorescent black light, **Syl/GE F8T5BLB**, which has a maximum output of 356 nm and a power rating of 8 W. The catalyst is either **Degussa P25** applied as a slurry and dried at 150° C or a 4000 **A** thick anatase film deposited from a spray of titanium **tetraalkoxide** solution [9]. The catalyst films made **from P25** are opaque to the wavelengths of interest. The thin films transmit about 50% of the incident light. Lamp output is measured with a UVP Black Ray 3221 radiometer.

The **FTIR** is a **Nicolet Model 8220** gas analyzer equipped with a Methods Development System and a 10 m **multipass** sample cell. Calibration curves for the gases of interest are prepared using NIST traceable standard gas **mixtures**.

## 3. RESULTS

The compounds dichloroacetyl chloride (**DCAC** or  $\text{CHCl}_2\text{COCl}$ ), carbon monoxide (**CO**), carbon dioxide ( $\text{CO}_2$ ), hydrogen chloride (**HCl**), carbonyl chloride (phosgene or  $\text{COCl}_2$ ), and unreacted TCE are detected in the gas exiting the photoreactor. The concentrations were quantitatively determined by on-line **FTIR**

using a long-path-length flow cell following the reactor. This avoids sampling and dilution errors. Representative spectra for the reactor exit stream and TCE, DCAC, and  $\text{COCl}_2$  are shown in Figure 2. The characteristic infrared absorption bands of the above mentioned compounds can be readily identified in the exit-gas spectrum. In separate experiments the same compounds have been identified by mass spectroscopy in a reactor system coupled to a molecular beam mass spectrometer (MBMS). The MBMS also established the presence of molecular chlorine,  $\text{Cl}_2$  among the products [10]. Symmetrical diatomic molecules cannot be detected by infrared spectroscopy, therefore  $\text{Cl}_2$  has not yet been directly quantified in this study. The concentrations of the various compounds in the exit gas stream are given in Table 1. Results are presented for a variety of residence times, percent conversion, and other experimental conditions. The concentrations are expressed as partial pressures in millitorr which can be converted to parts per million by volume (ppmv) by dividing by the initial pressure. For carbon the closure on the mass balance is usually within 5%. For chlorine the mass balances are low by significant amounts. The difference has been tentatively assigned to  $\text{Cl}_2$  since no other chlorine containing compounds are detected and the presence of molecular chlorine was unambiguously established in the MBMS experiments. This suggests that the yield of  $\text{Cl}_2$  may be as much as 30% of the chlorine content of the TCE destroyed under some conditions.

The data in Table 1 provide information about the sequence of chemical events that occurs in the destruction of TCE. At low residence times, ( $<0.003$  sec) most of the carbon (70%) from the destroyed TCE appears as DCAC. At longer residence times  $\text{CO}_2$  and phosgene are the major products. These trends are shown graphically in Figure 3 where the ratio of product concentration to TCE destroyed is plotted against residence time. The lines are a third order polynomial fit to the data and are included to illustrate trends. The data in Table 1 for reaction of DCAC establish that, under the photocatalytic reaction conditions, all the reaction products observed when TCE is destroyed are produced. Under similar conditions of light, catalyst, and residence time phosgene has been found to be stable.

#### 4. DISCUSSION

The appearance of phosgene among the products was surprising for two reasons: 1) Other workers have reported complete mineralization, and 2) it might have been expected to react with water vapor to give  $\text{CO}_2$  and  $\text{HCl}$ . However, in the homogeneous gas phase the reaction of phosgene with water is slow [11]. In addition the  $\text{TiO}_2$  surface in the reactor does not seem to be very active for the hydrolysis of phosgene. However, other surfaces have been found to be good catalysts for the reaction. For example, we have tested gamma alumina [12] and activated carbon [13] and have found them to efficiently catalyze the conversion of phosgene to  $\text{CO}_2$  and  $\text{HCl}$ . The reason others have not detected phosgene is

not clear; it could be the result of the analytical methods used. If one is trapping the gases by condensation, phosgene might hydrolyze in the trap. Or, reactive gases like phosgene and dichloroacetyl chloride might not pass through gas chromatography columns that are commonly used to analyze for TCE.

The results reported here are consistent with a situation in which at least 70% of the TCE that is destroyed is **first** converted to dichloroacetyl chloride. **Extrapolation** of the yields of DCAC to very short residence times suggest that about 30% of the TCE that is destroyed may react by a second pathway. This has not yet been **confirmed** by other evidence. The DCAC which is produced in the initial reaction step is then converted to the other products that have been found. The rate of destruction of DCAC is about 10% that of TCE [10]. Results showing the stability of phosgene under the photocatalytic reaction conditions suggest that direct photolysis of  $\text{COCl}_2$  is not the source of CO and Cl.

The products observed in this study are the same as those found in the homogeneous gas phase oxidation of TCE. The similarity may have implications for the mechanism of the reaction [ 14, 15]. This is the subject of other work underway in our laboratory.

In the work published to date the existence of **significant** quantities of by-products has not been reported for the photocatalytic oxidation of TCE in air streams. Our results show that under the well-defined operating conditions of our reactors, phosgene, CO, and very likely Cl, are produced in the early stages of oxidation. These findings require that any processes based on the photocatalytic oxidation of chlorinated **organics** insure that these substances are removed before the exhaust gases are released to the atmosphere.

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Table 1. Experimental Data

TCE Data

FEED mTorr TCE	FEED mTorr WATER	PROD mTorr TCE	PROD mTorr CO2	PROD mTorr co	PROD mTorr COCl2	PROD mTorr DCAC	PROD mTorr HCL	CONV TCE %	RES TIME s	RATE umol s m2	CARBON BAL %	CL BAL %
57	1002	31	19	10	16	2	6	46%	1.81E-1	23.09	96%	79%
57	1002	30	19	10	16	2	6	47%	1.81E-1	23.31	96%	78%
53	998	12	31	15	29	2	2	77%	4.53E-1	14.07	97%	65%
53	1002	21	23	12	22	2	2	60%	2.46E-1	20.25	97%	73%
53	1000	25	20	11	19	2	2	53%	2.04E-1	21.45	98%	77%
50	0	33	7	5	8	5	7	35%	1.04E-1	26.8	95%	90%
62	1088	20	28	16	27	3	4	68%	3.64E-1	18.3	94%	68%
53	0	42	3	3	2	5	11	20%	4.73E-2	35.1	96%	99%
54	1000	45	4	3	3	3	8	17%	4.75E-2	30.9	98%	97%
54	25050	32	12	8	15	3	15	40%	1.81E-1	18.9	98%	93%
39	0	31	3	2	2	3	2	19%	4.75E-2	24.3	97%	93%
53	0	44	3	2	2	4	3	17%	4.76E-2	31.0	97%	94%
60	0	47	4	3	3	7	1	22%	7.48E-3	42.3	98%	93%
46	0	31	5	3	4	6	2	33%	9.17E-3	39.7	92%	86%
54	0	42	4	3	3	5	1	22%	6.86E-3	42.0	96%	92%
62	0	56	2	1	1	3	1	9%	3.26E-3	41.3	99%	98%
52	0	49	1	1	1	2	1	7%	2.25E-3	41.0	99%	97%
60	0	47	4	3	3	7	1	22%	7.48E-3	42.3	98%	93%
46	0	31	5	3	4	6	2	33%	9.17E-3	39.7	92%	86%
54	0	42	4	3	3	5	1	22%	6.86E-3	42.0	96%	92%
52	0	36	5	4	4	7	2	31%	9.53E-3	40.0	94%	88%
62	0	56	2	1	1	3	1	9%	3.53E-3	38.1	99%	98%
52	0	49	1	1	1	2	1	7%	2.43E-3	37.9	99%	97%
50	0	42	3	2	2	4	1	16%	5.26E-3	35.5	100%	96%
53	0	44	3	3	3	5	1	17%	6.40E-3	32.6	101%	97%
a	0	59	2	1	1	3	1	8%	3.70E-3	35.0	100%	99%
54	0	44	3	2	2	4	1	18%	5.78E-3	40.3	96%	93%
469	0	458	2	2	3	7	1	2%	2.64E-3	96.9	100%	100%
291	0	282	2	2	3	6	1	3%	2.64E-3	88.0	100%	100%
193	0	184	2	1	3	6	1	5%	2.64E-3	80.2	100%	99%
50	0	42	2	1	2	5	1	15%	2.65E-3	66.0	100%	98%

DCAC DATA

FEED mTorr WATER	FEED mTorr DCAC	PROD mTorr co2	PROD mTorr co	PROD mTorr COCl2	PROD mTorr DCAC	PROD mTorr HCL	CONV DCAC %	RATE umol s m2	RES TIME s	CARBON BALANCE %	CL BALANCE %
0	36	7	3	4	32	9	12%	3.77	1.807-1	106%	104%
0	44	6	2	3	40	8	10%	3.65	1.80E-1	103%	101%

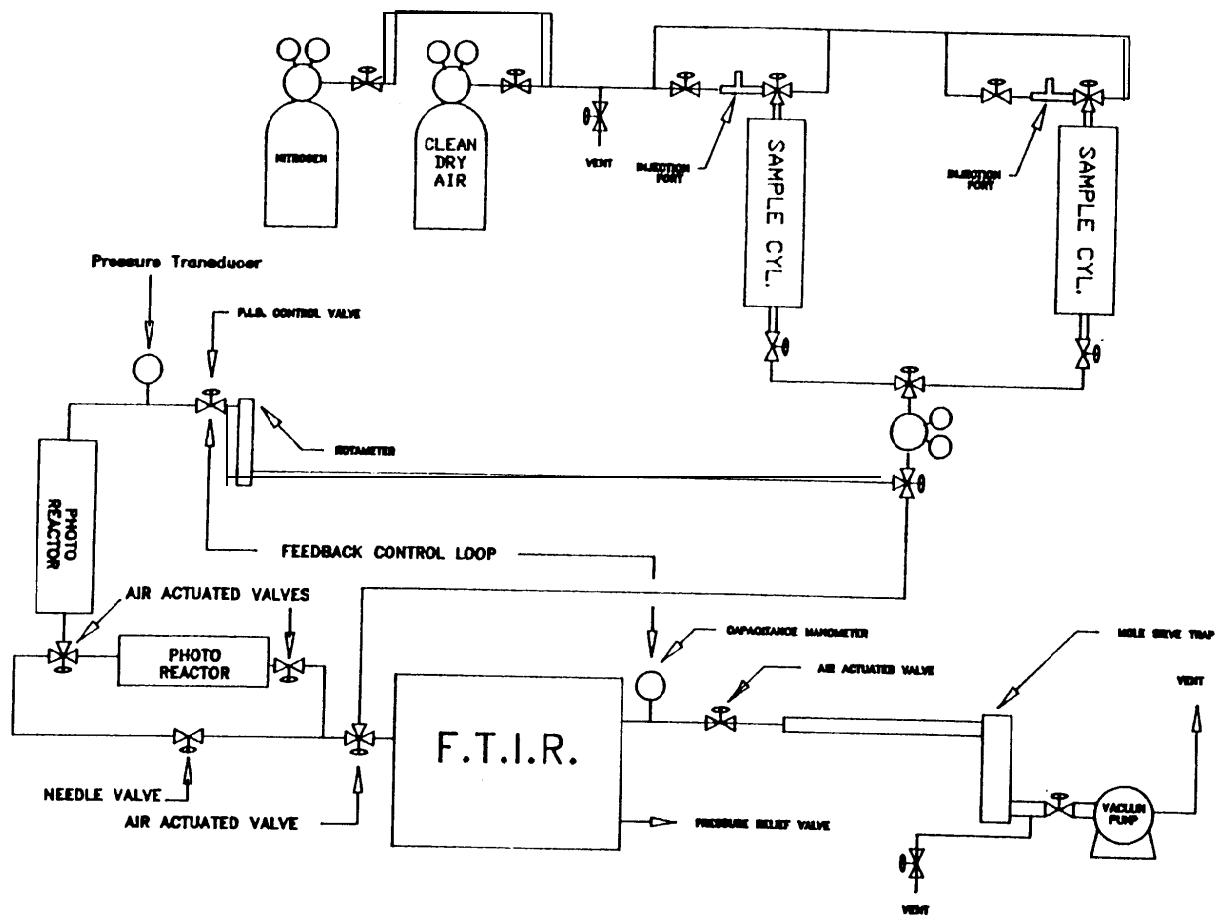


Fig. 1. Schematic of Experimental Apparatus



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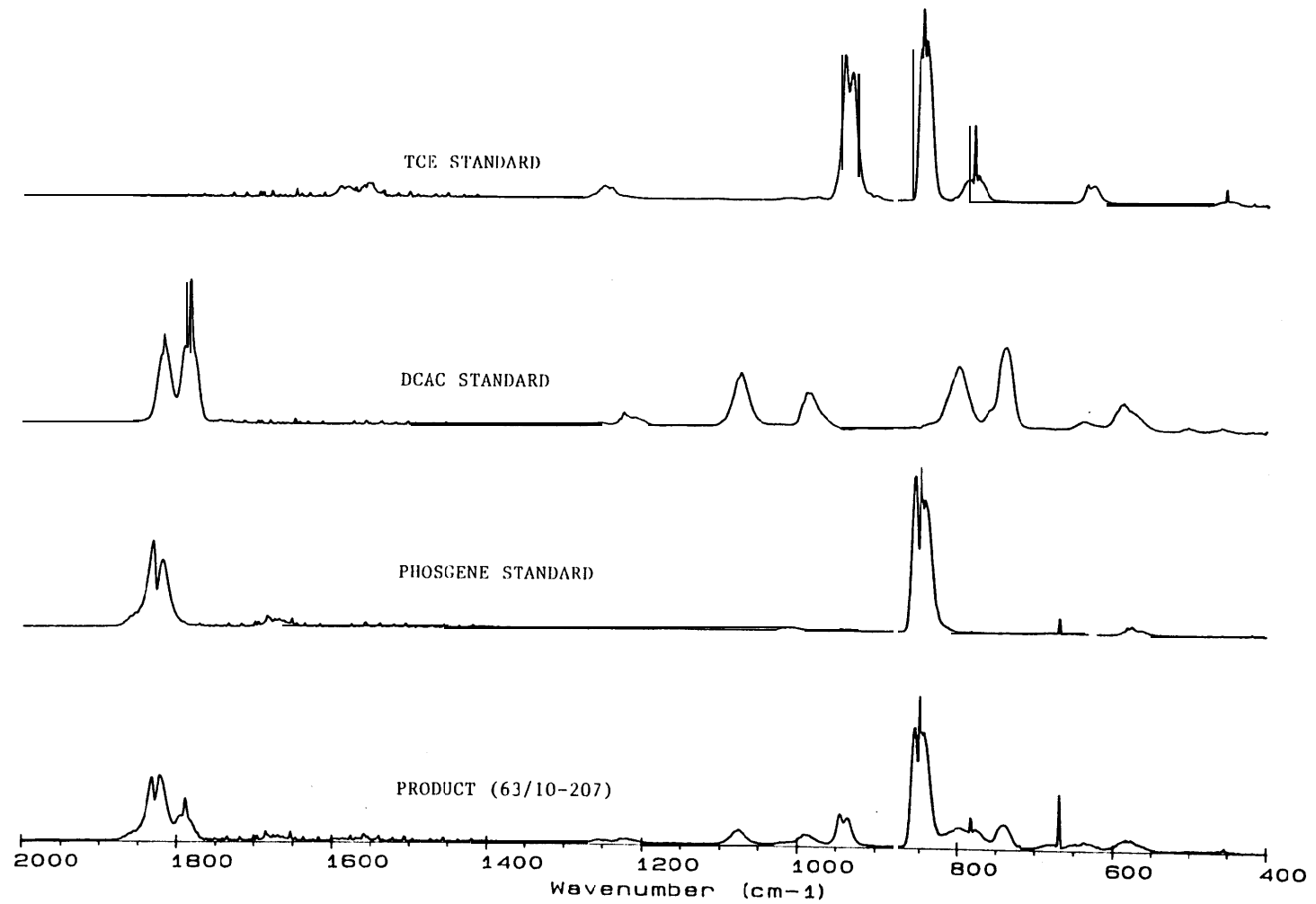


Fig. 2. Infrared Spectra of Reactants and Products

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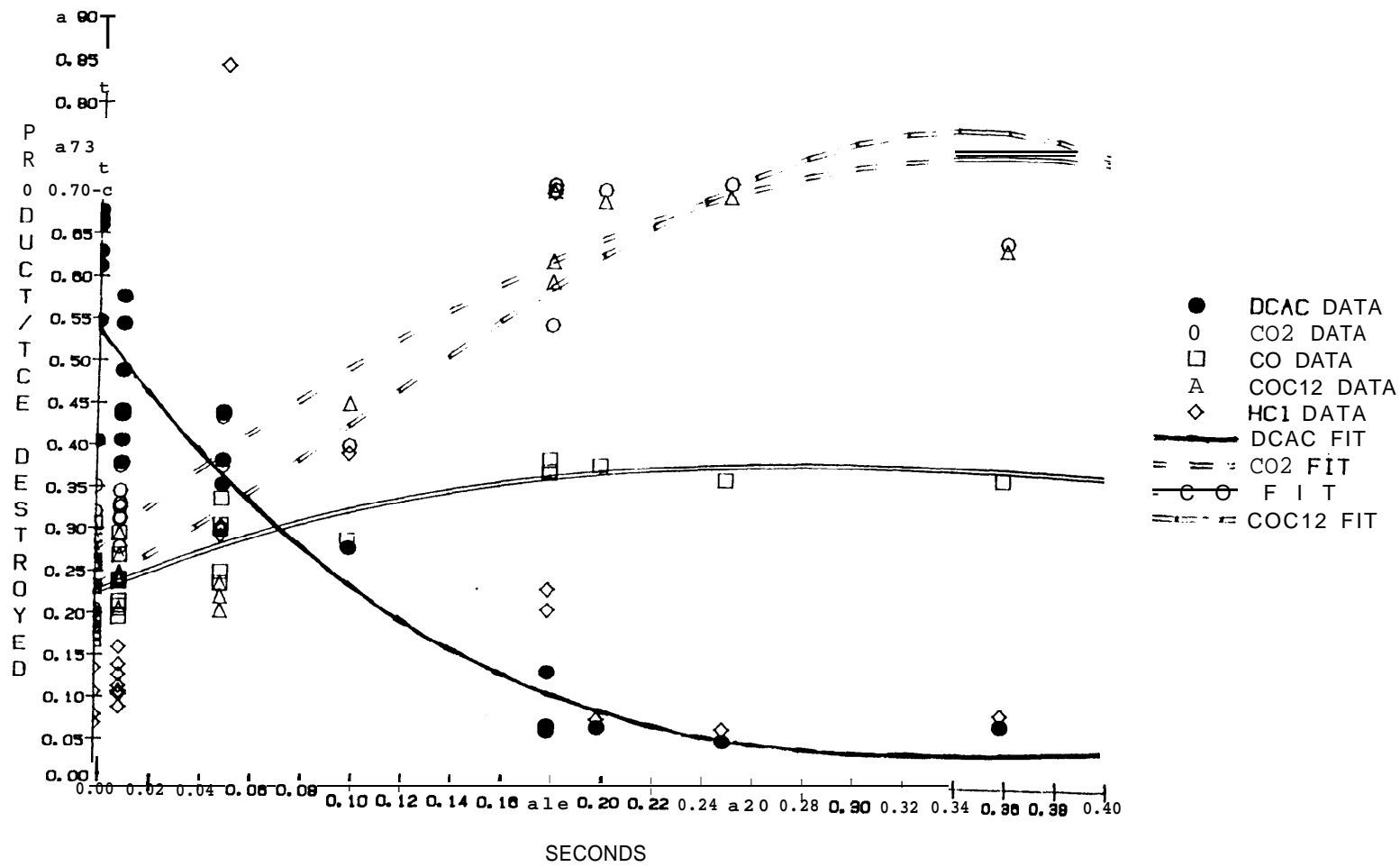


Fig. 3. (Product)/(TCE Destroyed) vs. Residence Time