Effect of Wall Deposit on Photochlorination Kinetics

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Several references (*2*, *3*, *4*, *9*) in the literature have given evidence of wall deposits in photochlorination of hydrocarbons in the gas phase. Sometimes the deposit has been observed directly as a brown (*9*) or yellow-brown (*2*) coating on the reactor wall, and at other times (*3*) there has been no visual evidence but simply a decrease in reaction rate. In the photochlorination of propane it was found (*2*) that the deposit increased with light intensity and/or conversion.

The expected effect of the deposit is to reduce the light intensity, which in turn lowers the reaction rate. To our knowledge the reduction in rate has not been measured quantitatively, although the phenomenon has been used to define conditions where there is no deposit. For example, the operating-cleaning cycle has been adjusted (*2*) on the basis of observing when the rate, at a set of standard conditions, began to decrease. From a kinetic standpoint two factors in addition to the opacity of the deposit may be important: (1) the effect of the wall deposit on the significance of heterogeneous termination steps and (2) the change in spectral distribution of the light passing through the deposit and the resultant effect on the reaction rate. The work reported here was designed to answer the first point. Rates of reaction and light intensities were measured for the photochlorination of propane in a steady-flow tubular reactor with and without wall deposits. To minimize the second factor, radiation from the lamp was passed through filter solutions to give light of a narrow wave-length range.

EXPERIMENTAL PROCEDURE

The apparatus and procedure were similar to those employed earlier (*2*). The elliptical reactor-lamp-reflector system was enlarged and modified by providing a separate jacket around the 2-mm I.D. quartz reactor tube for each filter solution (Figure 1). This greatly increased the stability of the filter solutions with respect to transmission of light. Chlorination reaction rates and light intensities at the inside wall were measured in the same reactor. The actinometer reaction used was the decomposition of oxalic acid activated by uranyl ions. The stability of the energy output of the lamp (General Electric UA-3, Uviarc) was checked periodically with a thermopile mounted flush with the elliptical wall of the reflector. The irradiated length of the reactor was 10.0 cm. for all runs. All of the reactor except this section was coated with black paint.

Rate and light were measured under three conditions: a clean reactor and two severities of wall deposit. The procedures followed for obtaining reproducible data were those developed earlier (*2*). It was found that a long preliminary operating time was necessary with the new, clean reactor and new lamp before reproducible results were achieved. This is probably due to the initial variation in light intensity with a new lamp and to a wall-conditioning effect, also observed by others (*3*, *4*, *9*). The experiments, after reproducibility was obtained, were run in the following sequence. Starting with a clean reactor, actinometer runs were performed, and then chlorination runs were made with progressively higher chlorine concentrations, from 0.61 to 2.67 mole % (the remainder was propylene in excess, 5.2 mole %, and nitrogen) in the feed gas. The total feed rate was maintained approximately constant for all runs at 8.7 cc./sec. (30°C., 780 mm). These clean-reactor chlorinations required 15 hours of radiation time. Then actinometer runs were made to establish the light intensity. After the reactor was dried by flowing nitrogen through it, but not cleaned, the chlorine concentration was adjusted to 2.67% and the lamp operated continuously for 75 hours to establish a modest wall deposit. Immediately afterward chlorinations were run at low chlorine concentrations (0.61-2.67 mole %) to establish rates of reaction. Then actinometer measurements were made to determine the intensity at the inside wall of the reactor in relation with the wall deposit.

After this sequence, the deposit was removed by washing the reactor with an alcoholic solution of potassium hydroxide, rinsing with distilled water, alcohol, and ether, and finally drying with nitrogen flow for several hours. The nitrogen also

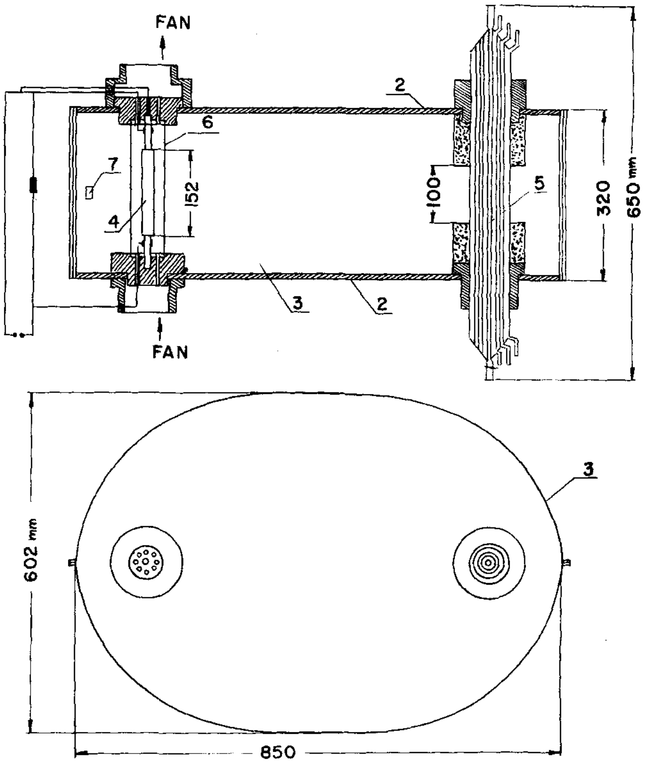
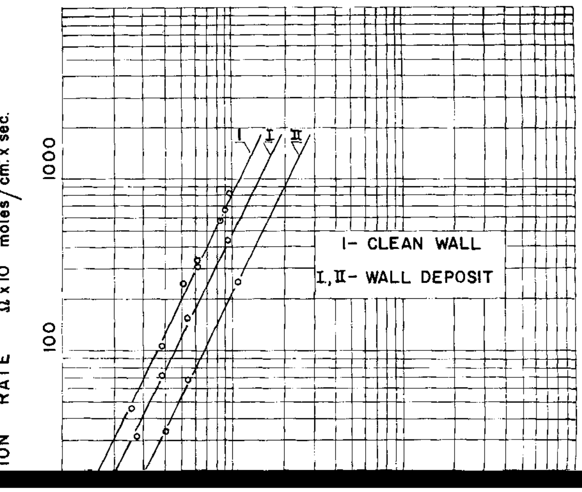


Fig. 1. Elliptical reactor system.

Table 1. Filter Solutions Employed

Jacket	Length of light path, mm.	Aqueous filter solution	Concentration, g.-moles/liter
Inner	10.5	$NiSO_4 \cdot 6H_2O$	1.50
Intermediate	5.5	$CuSO_4 \cdot 5H_2O$	0.25
Outer	7.5	$CoSO_4 \cdot 6H_2O$	0.50



served to remove oxygen from the wall surface. Actinometer runs were again made with the clean wall. Then a deposit was again established by chlorinating with a feed gas of 2.67 mole % chlorine, this time for 290 hours. Following this the rate was measured with low chlorine concentration runs and the intensity with a final set of actinometer measurements.

The requirements for accurate results established previously

[redacted]

TABLE 2. LAMP, FILTER SOLUTION, AND ACTINOMETER SOLUTION PROPERTIES

Wave length, Å	$F_\lambda \times 10^6$, Einsteins/ sec.	$F_\lambda/F_{tot} \times 10^2$	Actinometer Solution μ_λ, cm.$^{-1}$	Φ_λ, g.-moles/Einstein	Filter solutions, $\theta_\lambda \times 10^2$	Chlorine $\alpha_\lambda \times 10^{-4}$ sq.cm./g.-mole
2,250	1.354	1.02	179.20	0.560	0.00	
2,350	1.789	1.35	123.98	0.585	0.00	
2,450	3.093	2.34	94.67	0.597	0.00	
2,550	8.380	6.32	63.56	0.600	0.00	
2,650	6.519	4.92	56.69	0.590	0.00	
2,750	0.759	0.58	45.08	0.595	0.00	
2,850	4.383	3.31	30.48	0.588	0.25	2.533
2,950	4.367	3.29	20.06	0.584	4.25	5.297
3,050	8.239	6.22	14.19	0.578	38.00	9.212
3,150	17.961	13.55	9.02	0.573	46.20	13.127
3,250	0.869	0.65	5.30	0.565	43.25	14.970
3,350	1.820	1.37	3.72	0.550	30.75	14.970
3,450	0.490	0.36	1.80	0.532	18.25	11.054
3,550	0.890	0.67	0.90	0.516	6.00	9.442
3,650	29.762	22.45	0.45	0.503	0.40	6.448
3,750	0.940	0.71	0.41	0.500	0.00	
3,900	2.446	1.85	0.36	0.528	0.00	
4,050	11.845	8.94	0.36	0.565	0.00	
4,200	1.088	0.82	0.34	0.585	0.00	
4,350	22.194	16.74	0.32	0.595	1.25	1.612
4,900	3.360	2.54	0.02	0.215	2.00	
	= 132.600					

Actinometer summation, Equation (2): $\sum_{\lambda} \theta_\lambda \Phi_\lambda \frac{F_\lambda}{F_{tot}} [1\text{-exp}\,(-2R\mu_\lambda)] \doteq 4.484 \times 10^{-2}$g .-moles/Einstein

anism was proposed which fit these experimental observations and led to the following equation between the overall photochemical rate constant K and k_o:

$$K = \frac{k_o}{4\, I_{w,\,tot} \sum_{\lambda} \theta_\lambda \alpha_\lambda\, (F_\lambda/F_{tot})} \qquad (5)$$

The summation in the denominator was constant for all the runs and, when the data in Table 2 were used, equal to 11.82×10^3 cm.^{2}/g.-mole. Equation (5) expresses the direct proportionality between k_o and $I_{w,\,tot}$, since K, representing a combination of rate constants for individual steps in the chain-reaction mechanism, is independent of light intensity. Values of K calculated from Equation (5), and shown in Table 4, are nearly constant for all wall conditions. This means that the only effect of wall deposits was that due to a reduction in light intensity. Under the conditions of this study, the deposit did not influence the reaction mechanism or the values of the rate constants for the individual steps. If heterogeneous termination steps at the wall do influence the overall rate, wall deposits have no effect on these heterogeneous processes. Otherwise K would change; for example, if the deposit enhanced the rate of the heterogeneous steps, K would have decreased.

Equation (5) can be derived on the assumption that either (1) the only significant termination step is the homogeneous, first-order destruction of propyl radicals or (2) the controlling termination step is the heterogeneous reaction of propyl radicals at the wall. Because of this dual possibility, unequivocal statements cannot be made about the importance of heterogeneous termination steps. Thus the observed lack of influence of wall deposit on K would be expected if only homogeneous termination processes were significant. However the small diameter (2 mm.) of the reactor makes homogeneous terminations less likely. This conditional answer to the first point, raised at the beginning of this communication, is all that can be extracted from the data.

The wall-conditioning period, which we and others have observed, deserves some comment. In the preliminary period K increased slowly for the first 20 hours from 0.2×10^9 to 1.0×10^9 cc./Einstein. After about 80 hours it reached an average value of 1.59×10^9. From then on, K for a clean wall remained essentially constant even though the reactor was washed periodically in the manner described. Also, nearly the same value was obtained when wall deposits existed. A possible explanation for this behavior is that an invisible film (in contrast to the visible wall deposit) is formed by the attack of propyl radicals on the quartz wall surface, producing Si-O-C_3H_8 linkages.

TABLE 3. ACTINOMETER RESULTS

Wall condition	t_o, °C.	t_L, °C.	$Q \times 10^2$, cc./sec.	$C_o \times 10^6$, g.-moles/cc.	$C_L \times 10^6$, g.-moles/cc.	Conversion, %	$r_A \times 10^7$, g.-moles/ (cc.)(sec.)	$I_{w,\,tot} \times 10^7$, Einsteins/ (sq.cm.)(sec.)
Clean	29.0	29.0	4.05	4.955	4.877	1.56	1.00	1.11
Wall deposit I (75 hr.)	29.6	29.6	1.17	4.955	4.797	2.64	0.59	0.657
Wall deposit II (290 hr).	29.4	29.5	3.95	4.989	4.966	4.97	0.28	0.312

Table 4. Chlorination Data and Rate Constants*

$I_{w,tot}$ $\times 10^7$, Einsteins/ (sq. cm.) (sec.)	N_2, mole %	Propane, mole %	Cl_2, mole %	$(Cl_2)_o$ $\times 10^6$ moles/cc.	$(Cl_2)_L$ $\times 10^6$, moles/cc.	$\Omega \times 10^8$, moles/ (cc.) (sec.)	Conversion of Cl_2, %	Error in mass balance, %	Wall condition	$k_o \times 10^{-7}$, cc./ (sec.) (mole)		$K \times 10^{-9}$, cc./Einstein	
1.114	94.12	5.25	0.63	0.2602	0.2434	46.22	6.44	1.10	Clean	0.72		1.38	
	93.80	5.24	0.96	0.3987	0.3593	108.61	9.88	2.27		0.75		1.44	
	93.44	5.21	1.35	0.5569	0.4669	241.69	15.64	0.46		0.91		1.75	
	93.16	5.20	1.64	0.6754	0.5621	314.06	16.78	0.26		0.82	(avg. 0.83)	1.57	(avg. 1.59)
	93.16	5.20	1.64	0.6778	0.5567	335.68	17.87	0.27		0.88		1.69	
	92.55	5.16	2.29	0.9456	0.7376	379.61	22.00	0.06		0.82		1.58	
	92.34	5.15	2.46	1.0176	0.7814	658.16	23.18	0.31		0.79		1.51	
	92.19	5.14	2.67	1.1059	0.8074	832.23	26.94	0.61		0.92		1.77	
0.657	94.08	5.25	0.67	0.2768	0.2654	31.35	4.15	2.90	Wall Deposit I	0.42		1.37	
	93.01	5.23	0.46	0.3941	0.3686	70.38	6.46	1.20		0.48	(0.49)	1.55	(1.59)
	93.45	5.21	1.34	0.5530	0.4964	156.78	10.24	1.51		0.56		1.82	
	92.39	5.15	2.46	1.0131	0.8556	439.43	15.54	0.28		0.51		1.63	
0.312	92.19	5.14	2.67	1.1043	1.0143	251.60	8.15	1.47	Wall Deposit II	0.21		1.52	
	94.14	5.25	0.61	0.2526	0.2480	12.65	1.82	0.58		0.19	(0.21)	1.38	(1.46)
	93.77	5.23	1.00	0.4105	0.3983	33.66	2.97	0.07		0.20		1.40	
	93.44	5.21	1.35	0.5569	0.5325	67.48	4.36	0.44		0.22		1.54	

* All runs were at approximately constant temperature (30°C.), pressure (780 mm. Hg), and flow rate (8.7×10^3 cc./sec.), corresponding to a Reynolds number of 390.

Perhaps the existence of such a film could be verified by X-ray diffraction analysis. Chambers and Ubbelohde (3) advanced this postulate in accounting for the effects of an invisible layer. If heterogeneous terminations are significant, they could be hindered by these linkages. Thus the overall rate constant K would increase until an equilibrium surface condition is achieved where no more net reaction of propane with the wall occurs. These silica linkages may not be readily soluble in the alkali, alcoholic solution, thus explaining the constant value of K despite washing. According to this explanation, the visible layer added onto the invisible film must not affect the rate of the termination steps, but only reduce the light intensity.

If heterogeneous termination is assumed in deriving Equation (5), K is a function of reactor diameter while for homogeneous termination it is not. Hence more insight into the importance of wall terminations could be obtained by measuring chlorination rates in reactors of different diameters with and without wall deposits.

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NOTATION

C = concentration, g.-moles/cc.; concentration of chlorine also denoted as (Cl_2).
F_λ = energy flux from the lamp of wave length λ; F_{tot} = total flux; Einsteins/sec.
$I_{w,tot}$ = total light intensity reaching inside wall of reactor, from one side, Einsteins/(sq.cm.) (sec.)
k_o = second-order rate constant, (cc.)/(g.-mole) (sec.)
K = overall photochemical rate constant, cc./Einstein
L = irradiated length of reactor, cm.
P = pressure, mm. Hg
Q = volumetric flow rate, cc./sec.
r_A = rate of disappearance of oxalic acid in actinometer reaction, g.-moles/(cc.) (sec.)
R = radius of reactor tube, cm.
t = temperature, °C.
V_R = reactor volume, cc.
x_{Cl_2} = conversion of chlorine

Greek Symbols

α_λ = molal absorptivity of chlorine at wave length λ, defined as $\alpha = -\ln \dfrac{I/Io}{Cd}$, sq.cm./g.-mole
λ = wave length of radiation, Å
μ_λ = attenuation coefficient of actinometer solution, cm.$^{-1}$
θ = fraction of incident light transmitted by filter solutions
Ω_{Cl_2} = rate of formation of Cl_2 in chlorination reaction, g.-moles/(cc.) (sec.)
Φ = quantum yield of actinometer reaction, g.-moles/Einstein

Subscripts

o = reactor inlet
L = reactor outlet
w = wall
m = arithmetic mean of inlet and outlet values

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