TABLE I

CHLORINATION OF CH_3CHF_2 AND $CH_3CCl F_2$ AS A FUNCTION OF CHLORINE CONCENTRATION

Temperature, 200°. Illumination, two 500-w. incandescent bulbs

Run	Cl_2/ethane	Contact time,[a] min.	Yield,[b] g.	Conversion, %	Product composition, weight % $CH_2ClCClF_2$	$CHCl_2CClF_2$	CCl_3CClF_2
			Feed: CH_3CHF_2				
1	8.0:1	0.6	122	43			95
2	4.5:1	1.0	117	39			95
3	1.9:1	1.6	65	25	6	13	18	63
4	1.0:1	2.2	20	10	12	50	30	8
			Feed: $CH_3CCl F_2$				
5	3.8:1	1.1	80	40		5	10	85
6	1.6:1	1.8	71	36		7	13	80
7	1.0:1	2.2	63	31		10	16	74

[a] Based on reactants at 25°. [b] Grams of product boiling above room temperature per 100 g. of fluoroethane.

TABLE II

CHLORINATION OF $CH_3CCl F_2$ AS A FUNCTION OF TEMPERATURE

Illumination, one G. E. H-4 100-w. ultraviolet source

Run	Mole ratio Cl_2/ethane	Temp., °C.	Yield,[a] g.	Product composition, weight % CH_2Cl-$CCl F_2$	$CHCl_2$-$CCl F_2$	CCl_3-$CCl F_2$
1	6:1	125	19	11	18	70
2	5:1	175	38	8	12	80
3	5:1	200	55	6	14	80

[a] G. of product boiling above room temp. per 100 g. of chlorodifluoroethane.

found to occur in iron reactors at 200–400°, and the over-all reaction was that of the chlorination of 1-chloro-1,1-difluoroethane and its dehydrofluorination products, with the latter predominating.

Thus the conclusion may be drawn that iron(III) chloride is a specific catalyst for both dehydrofluorination and chlorination of 1-chloro-1,1-difluoroethane below the temperatures which McBee[2] found caused dehydrochlorination. Also, the effect of the iron concentration in the metal is easily seen. At 300° about 60% of the original fluorine was in the products obtained with the monel reactor, about 20% in those from the stainless steel, and only 10% in those from the iron reactor. The reaction initiates in each of the metals at about 200–225°, and becomes appreciable by 250°. Iron and stainless steel reactors cannot be used above the boiling point of iron(III) chloride, about 318°, but monel may be used to above 400°, where the reaction becomes uncontrollable.

Nitrogen dilution of the reactants modified the reaction somewhat, allowing the production of a slightly greater percentage of fluorine-containing material.

No evidence of dehydrofluorination was found during photochemical chlorination at temperatures below 200°, and the reaction gave the expected products. The temperature necessary for the initiation of the reaction was about 125°, and at 200° conversions greater than 40% were effected at one pass. In addition, chlorination at these temperatures gave appreciable amounts of di- and trichlorodifluoroethanes which are not obtained at higher temperatures.

No attempt was made to determine the amount of 1-chloro-1,1-difluoroethane formed when 1,1-difluoroethane was the starting material, as one preliminary distillation of the gaseous products indicated that very little 1,1-difluoroethane was unreacted. As when 1,1-difluoroethane was subjected to chlorine in direct sunlight,[6] no evidence has been found of any 2-chloro-1,1-difluoroethane, but small amounts of 2,2-dichloro-1,1-difluoroethane appeared when low chlorine-to-fluoroethane ratios were used.

By comparison of run 5, Table I, and run 3, Table II, it may be seen that only slight differences exist in the composition of the products obtained when using visible and ultraviolet light. A slightly lower yield was obtained in the illumination from the 100-w. ultraviolet source than in that from the two 500-w. incandescent bulbs.

(6) A. L. Henne, J. B. Hinkamp and W. J. Zimmerschied, THIS JOURNAL, **67**, 1906 (1945).

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The Preparation of Specific Adsorbants

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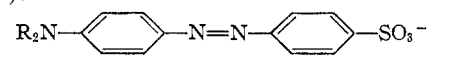
The preparation of specific adsorbants was first described by Dickey.[2] These adsorbants were silica gels, which, depending on the method of preparation, preferentially adsorbed a particular dye in the series methyl, ethyl, *n*-propyl and *n*-butyl orange (I).



I, R = methyl, ethyl, *n*-propyl or *n*-butyl

Emmett[3] repeated the measurements on samples of Dickey's gels which had been prepared seventeen months previously, and found evidence for specificity although the effects were much smaller, presumably as a result of the change in properties of the gels on standing.

Experimental

In the present investigation, gels were prepared by mixing 30 ml. of aqueous sodium silicate (*d* 1.401) and 0.2 g. of dye and diluting to 200 ml. To this mixture, 200 ml. of 0.2 *N* hydrochloric acid was added.[4] The preparations were allowed to sit at room temperature for eight days. (Gelation occurred on the fifth day.) The gels were then poured onto paper towels and dried in air for another eight-day period. The dried gels were ground and sieved, and the fraction between 60 and 200 mesh was continuously extracted with methanol at room temperature for three days. Although most of the dye was thereby removed, some coloration of the gel persisted. Subjecting the gels to extraction for a two-week period did not significantly diminish the in-

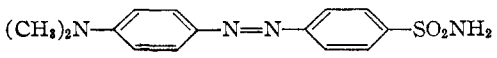
(1) American Cancer Society Postdoctorate Fellow, 1951–1952.

(2) F. H. Dickey, *Proc. Nat. Acad. Sci.*, **35**, 227 (1949).

(3) P. H. Emmett, private communication.

(4) Hydrochloric acid was found to give consistently better results than acetic acid. This has been independently discovered by Dickey (private communication). In one case, the dye (II) was added to the hydrochloric acid rather than the silicate solution. The sodium silicate dilution reported here is relatively high. *A priori*, it seemed that a high dilution and hence a slow gelation would be favorable for strong adsorption of the dye. Recent experiments seem to indicate the contrary.

tensity of color. A control gel containing no dye was prepared simultaneously with the other samples. The dyes used were methyl and ethyl orange (I), and *p*-diamino-*p'*-sulfonamidoazobenzene (II).



II

Tables I and II summarize the results of adsorption measurements on extracted gels, for three independent investigations (those of Dickey (A), Emmett (B), and the present work (C)). The concentrations of dye and amounts of gel were as follows: A, dye concn. = 1.5×10^{-5} *M* in 5% acetic acid, 1 g. gel; B, dye concn. = 3.0×10^{-5} *M* in 5% acetic acid, 1 g. gel; C, dye concn. = 0.5×10^{-5} *M* in 0.1 *N* hydrochloric acid, 0.25 g. gel.

Ten ml. of dye solution was used in each case. In the present investigation samples were shaken 24 hours on a high speed shaker. Longer shaking periods did not affect the results. All readings were made on a Beckman spectrophotometer at 5100 Å. In Table I

$$\text{Adsorption Power} = \frac{\text{Moles of dye adsorbed/g. of gel}}{\text{Moles of dye in solution/g. of solution}}$$

and in Table II

$$\%\ \text{excess adsorption} = \frac{\text{Adsorption power of gel-adsorption power of control}}{\text{Adsorption power of control}} \times 100$$

TABLE I

ADSORPTION POWER

Investigation	Gel prepared with	Adsorption power for Methyl orange	Ethyl orange	II
(A)	Control	84	80	...
	Methyl orange	300	128	...
	Ethyl orange	230	740	...
(B)	Control	5.6	5.2	...
	Methyl orange	11	7.2	...
	Ethyl orange	8.0	10	...
This paper	Control	18	9.2	31
	Methyl orange	100	32	144
	Ethyl orange	90	74	120
	II	106	34	168

TABLE II

% EXCESS ADSORPTION

Investigation	Gels prepared with	% Excess adsorption of Methyl orange	Ethyl orange	II
(A)	Methyl orange	250	60	...
	Ethyl orange	150	800	...
(B)	Methyl orange	100	40	...
	Ethyl orange	40	90	...
This paper[a]	Methyl orange	450	250	370
	Ethyl orange	380	700	290
	II	480	280	450

[a] In a previous experiment in this Laboratory, when the present techniques were not as yet developed, two gels prepared in the presence of methyl orange and II gave the following % excess adsorption for methyl orange, ethyl orange and II, respectively: Methyl orange gel, 80, 50, 90; gel (II), 90, 50, 120; each sample contained 10 ml. of 2.5×10^{-5} *M* dye and 0.5 g. of gel.

The new data are in agreement with the observations of Dickey.

It is of interest to note that specificity for II and methyl orange are closely parallel, indicating that a negative charge at the *p'*-substituent is not a requirement for specificity. Since the sulfonate and sulfonamido groups are nearly the same size, stereochemical specificity for the *p'*-substituent could not be investigated in this experiment. None of the gels would measurably adsorb methyl orange at *p*H 7.0.

The number of moles of methyl orange adsorbed onto the methyl orange gel was calculated, and the same quantity of dye was then adsorbed onto a control gel (by suitable increase of the initial dye concentration in solution). The intensity of color of the control gel after adsorption of the dye was qualitatively noted to be much less than that of the original methanol-extracted methyl orange dye, indicating that under the conditions of the adsorption experiments reported here less dye was adsorbed than was originally present in the gel, even under the most favorable conditions for adsorption.

Specific adsorbants for dyes of the methyl orange type can be readily prepared by a method similar to that of Dickey.[1] The dyes must contain a cationic center in order that the adsorption be measurable. The specificity of the gels has again been shown to be dependent on the stereochemical constitution of the *p*-substituent (dialkylamino group) of the dye. Although no stereochemical investigation of the *p'*-substituent has been made, the specificity has been found to be independent of a negative charge on this group.

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p-Amino- and *p*-Fluoro-β-phenylalanine

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Convenient methods are described for the preparation of *p*-amino- and *p*-fluorophenylalanine, which were required for biochemical experiments. *p*-Aminophenylalanine has been prepared by reduction of the easily available[2] *p*-nitro compound with stannous chloride and hydrochloric acid,[1] or from diethyl *p*-nitrobenzylacetamidomalonate.[3] Both by catalytic hydrogenation of *p*-nitrophenylalanine (yield 87%) and by reduction of the azlactone[4] from *p*-nitrobenzaldehyde and hippuric acid (yield 78%, calculated on the aldehyde), the amino acid is obtained in pure form.

For the preparation of *p*-fluorophenylalanine, the azlactone synthesis[5] and the condensation of diethyl acetamidomalonate with *p*-fluorobenzyl chlo-

(1) Scientific Department, Israeli Ministry of Defence, Tel-Aviv, Israel.

(2) E. Erlenmeyer and A. Lipp, *Ann.*, **219**, 213 (1883).

(3) J. H. Burckhalter and V. C. Stephens, THIS JOURNAL, **73**, 56 (1951).

(4) (a) R. L. Douglas and J. M. Gulland, *J. Chem. Soc.*, 2893 (1931); (b) H. Burton, *ibid.*, 1265 (1935).

(5) G. Schiemann and W. Roselius, *Ber.*, **65**, 1489 (1932).