

pared from the corresponding 3'-phosphate (I) by a method similar to the case of adenosine 5'-phosphorop-anisidate,<sup>5</sup> was allowed to react with excess isoamyl nitrite in an equal volume mixture of pyridine and acetic acid at room temperature, the phosphate I was obtained exclusively. In DMF solution the isoamyl nitrite treatment of II showed small amounts of N-debenzoylation and deamination. Therefore, this procedure was applied to the synthesis of a protected ribotrinucleotide with a 3'-phosphomonoester end group (IVb) which could be further condensed with a protected oligonucleotide block with a free 5'-hydroxyl group. Compound II (1 mmole) was condensed with 5'-O-monomethoxytrityl-N,2'-O-dibenzoylcytidine 3'-phosphate (III) (0.7 mmole) in pyridine using DCC as a condensing agent. After 4 days, the aqueous pyridine treatment was given overnight and the azeotropically dried pyridine solution of IVa was precipitated with ether. The precipitate was treated with isoamyl nitrite (10 mmoles) in a mixture of pyridine (5 ml) and acetic acid (5 ml) for 4 hr at room temperature. The nucleotides were precipitated in ether to remove pyridinium acetate. The precipitate was dissolved in pyridine and 95% ethyl alcohol and applied to a column of TEAE-cellulose (acetate form). The elution conditions and the pattern are shown in Figure 1. Peak VIII contained the pure dinucleotide (IVb). The yield was 3500 OD<sub>304</sub> units (0.2 mmole, 28%). The spectral properties in ethyl alcohol were  $\lambda_{\max}$  262 and 304 m $\mu$ ,  $\lambda_{\min}$  250 and 290 m $\mu$ , and  $\epsilon_{304}/\epsilon_{280} = 0.81$ ;  $\epsilon_{(p)}$  at 304 m $\mu$  was 8800. The purity was checked by paper chromatography and electrophoresis after partial removal of the protecting groups. Methanolic ammonia treatment gave MMTr-CpCp<sup>6</sup> ( $R_f$  0.27 in solvent A,<sup>7</sup>  $R_{Cp}$  0.80 in paper electrophoresis at pH 7.5). The benzoylated dinucleotide obtained by 80% acetic acid treatment showed  $R_f$  0.71 in solvent B and  $R_{Cp}$  0.81 in paper electrophoresis at pH 7.5. The acidic treatment and subsequent removal with ammonia gave the unprotected dinucleotide, CpCp ( $R_{Cp}$  0.43 in solvent A and  $R_{Cp}$  1.03 in paper electrophoresis at pH 7.5), which was completely degraded by pancreatic RNase.

For the synthesis of trinucleotide VIb, the protected dinucleotide IVb (3250 OD<sub>304</sub> units, 0.185 mmole) was allowed to react with N,O<sup>2'</sup>-dibenzoyladenosine 3'-phosphorop-anisidate (V) (3110 OD<sub>280</sub> units) and DCC in pyridine. Using essentially the same procedure as above, the protecting group in VIa was removed and the trinucleotide VIb, which was eluted at about 0.3 M salt concentration in TEAE-cellulose (acetate) column, was isolated in a yield of ca. 30% (1050 OD<sub>304</sub> units). The spectral properties in ethanol were  $\lambda_{\max}$  264 m $\mu$  and shoulder at 280 and 300 m $\mu$ ,  $\lambda_{\min}$  250 m $\mu$ , and  $\epsilon_{304}/\epsilon_{280} = 0.50$ . Ammonia treatment gave MMTr-CpCpAp ( $R_f$  0.14 in solvent A,  $R_{Cp}$  0.86 in paper electrophoresis at pH 7.5) and a

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(6) The system of abbreviations is essentially the same as used in the *Journal of Biological Chemistry*. The letter p at the right indicates 3'-phosphate and MMTr at the left means 5'-monomethoxytrityl group.

(7) Paper chromatography was performed using the descending technique. The solvent systems used were: solvent A, isopropyl alcohol-concentrated ammonia-water (7:1:2, v/v); solvent B, ethyl alcohol-1 M ammonium acetate, pH 7.5 (7.3, v/v); solvent C, saturated ammonium sulfate-water-isopropyl alcohol (79:19:2, v/v).

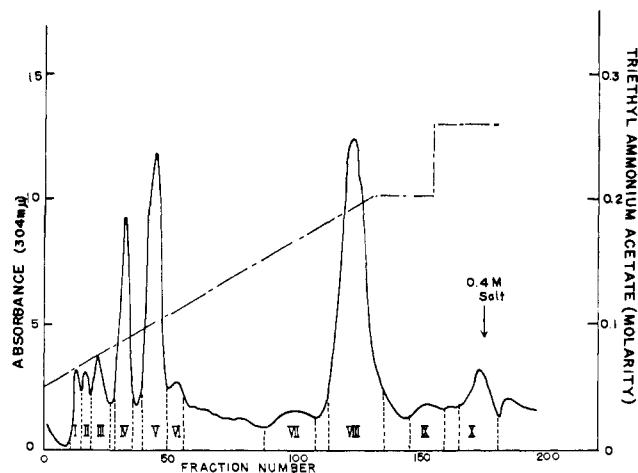


Figure 1. Chromatography of the products obtained in the synthesis of the dinucleotide IVb on a TEAE-cellulose (acetate) column (2.7 × 50 cm) preequilibrated with 95% ethanol. Elution was carried out using a linear salt gradient of triethylammonium acetate (pH 6.5) in 95% ethanol (2 l. of 0.05 M salt in the mixing vessel and an equal volume of 0.25 M salt in the reservoir). Fractions of 21 ml were collected every 15 min. Peak VIII contained the dinucleotide IVb.

trace of a trityl-negative side product. The benzoylated trinucleotide showed  $R_f$  0.79 in solvent B,  $R_{Cp}$  0.81 in paper electrophoresis at pH 7.5. The completely deprotected trinucleotide CpCpAp ( $R_{Cp}$  0.14 in solvent A and  $R_{Cp}$  1.03 in electrophoresis at pH 7.5) was degraded with pancreatic RNase to give cytidine phosphate ( $R_f$  0.73) and adenosine 3'-phosphate ( $R_f$  0.17) in the ratio of 2.03:1.00 in solvent C.

Thus the properly protected ribotrinucleotide with 3'-phosphate was obtained in quantity using the anisidate protection. Further condensation of the trinucleotide with oligonucleotide blocks having free 5'-hydroxyl groups and polymerization of the de-tritylated trinucleotide are in progress.

Application of this method for the protection of 5'-phosphomonoester in the synthesis of deoxyribo-polynucleotides and the use of phosphoramidates with different stabilities are under investigation.

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### Catalytic Formation of Hydrocarbons (C<sub>1</sub>-C<sub>5</sub>) from Hydrogen and Carbon Monoxide over the Electron Donor-Acceptor Complex Films of Alkali Metals with Transition Metal Phthalocyanines or Graphite

Sir:

Various phthalocyanine films and graphite exhibit marked catalytic activities for hydrogen exchange, hydrogenation of unsaturated hydrocarbons,<sup>1</sup> and isomerization of butenes<sup>2</sup> at room temperature when they are

(1) M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, *J. Catal.*, **9**, 418 (1968).

(2) M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, **63**, 2012 (1967).

Table I. Preparation of Hydrocarbons (C<sub>1</sub>-C<sub>5</sub>) over Various Phthalocyanine-Sodium EDA Complexes and Graphite-Sodium Complex

Acceptor (g)	Donor (g)	H <sub>2</sub> , cm	CO, cm	Temp, °C	Total amt of hydrocarbons, ml	% <sup>a</sup>				
						C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>
Fe-Pc	Na	45	15	240	18	4	89	5	2	0
(0.2)	(0.5)	45	15	170	1.9	38	59	3	1	0
Co-Pc	Na	45	15	240	11	6	91	3	1	0
(0.2)	(0.5)	45	15	180	1.8	58	38	4	0	0
Pt-Pc	Na	46	12	220	10.2	2	82	9	6	1
(0.2)	(0.5)									
H <sub>2</sub> -Pc	Na	45	15	240	2.4	10	84	6	0	0
(0.2)	(0.5)									
Graphite	Na	40	10	300	1.4	2	74	22	2	0
(5)	(2)									

<sup>a</sup> C<sub>1</sub>, methane; C<sub>2</sub>, ethylene + ethane; C<sub>3</sub>, propylene + propane; C<sub>4</sub>, 1-butene + *cis*-2-butene + *trans*-2-butene + butane; C<sub>5</sub>, pentane, 1-pentene.

brought into contact with sodium or potassium, resulting in the formation of the electron donor-acceptor (EDA) complexes. It has been also demonstrated that the catalytic formation of ammonia from N<sub>2</sub> and H<sub>2</sub> takes place appreciably over the transition metal-Pc (phthalocyanine) or graphite complexes with alkali metals (Na or K) under mild conditions.<sup>3</sup>

The deeply colored stable EDA complex films were prepared by the successive evaporation of each of the phthalocyanines (Fe, Co, Ni, Mo, Pt, and H<sub>2</sub>) and sodium on the wall of the reaction vessel similarly as described previously.<sup>1-3</sup> The graphite-Na (or K) complex was also obtained in the reaction between graphite powder and distilled sodium or potassium. Carbon monoxide (20 cm of Hg) was sorbed to a considerable extent on each EDA complex film in the temperature range between 25 and 200°, but the desorption proceeded very slowly even at higher temperatures such as 200°. When hydrogen (20 cm of Hg) was admitted at 170° onto the complex films which preadsorbed CO, a considerable amount of hydrogen was taken up<sup>4</sup> and a mixture of hydrocarbons such as ethane, ethylene, and propane was detected by gas chromatography in a closed circulating reaction system (140 ml).

A mixture of CO and H<sub>2</sub> with various relative molar ratios reacted over each phthalocyanine EDA complex film with excess sodium in the temperature range between 25 and 260°. Various kinds of hydrocarbons (C<sub>1</sub>-C<sub>5</sub>) were formed at temperatures above 90° in 20 hr. The amount of hydrocarbons and the distribution of the products (in the steady state) are shown in Table I. It was found that when the portion of CO in the CO-H<sub>2</sub> mixture was increased, the yield of the hydrocarbons decreased markedly, probably because CO retarded hydrogen activation by the complex films.

It was interesting to note that a small amount of methanol and ethanol and a trace of CO<sub>2</sub> were detected in the product at lower temperatures such as 120° under CO-rich conditions over Fe-, Mo-, and Pt-Pc complex films. A trace of water was obtained in each run even at higher temperatures. The reactivity of the complexes did not change appreciably in several runs. The amount of higher hydrocarbons (C<sub>3</sub>-C<sub>5</sub>) increased considerably at

240° over the Fe-Pc complex film when the content of CO in a mixture gas was increased. It was also found that the amount of methane increased in the reaction at lower temperatures under hydrogen-rich conditions. The product distributions were not so appreciably dependent upon the sorts of the central metal ions of each phthalocyanine except that methane was produced to a greater extent over the Fe-, Co-, or Mo-Pc EDA complex than the other complex films under similar reaction conditions.

Similar hydrocarbons were also formed when a mixture of CO and H<sub>2</sub> was admitted to the graphite-Na (or K) complex in the temperature range between 200 and 350°.

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### Temperature Dependence of the Reaction Yields from Recoil Tritium Reactions. I. Energetics of Tritium Atom Addition to Olefins

Sir:

Chemical processes initiated by very high kinetic energy atoms have correspondingly lesser requirements for initial thermal excitation energy in the struck molecule, and a lack of dependence of reaction rate upon temperature is frequently cited as proof of the "hot" atom character of the reactions.<sup>1,2</sup> Earlier searches for a temperature dependence in recoil tritium reactions have either failed to detect any change in yield vs. temperature,<sup>3,4</sup> or else have simultaneously involved both phase and temperature changes.<sup>5,6</sup> We have now observed and measured both the temperature and pressure effects on the decomposition

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(5) E. K. C. Lee and F. S. Rowland, *J. Inorg. Nucl. Chem.*, **25**, 133 (1963).

(6) B. G. Dzantiev and A. P. Schvedchikov, "Chemical Effects of Nuclear Transformations," Vol. 1, International Atomic Energy Agency, Vienna, 1965, p 87.

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(4) CO and H<sub>2</sub> adsorptions took place negligibly over each phthalocyanine or sodium film alone in the temperature range studied.