is reported by Biltz and Balz[4] who measured the dissociation pressure of various ammonia salts and found that these pressures alternated as the series was ascended. An alternation in the yield of Grignard reagents with alkyl iodide chain length has been reported by Gilman and McCracken.[5]

In general, metal cutting is accompanied by a high surface temperature, high pressure between the moving surfaces and the production of a considerable area of clean, highly reactive surface. Fluid film formation, common to ordinary types of lubrication, plays no part in metal cutting. The mechanism of cutting fluid action is obviously a problem in the extreme boundary region of lubrication. While much evidence has accumulated to uphold the role of adsorbed surface films in reducing the frictional resistance of sliding surfaces under relatively mild boundary lubrication conditions,[6,7,8] another mechanism is believed to obtain in the extreme boundary region of lubrication.[9] In the extreme boundary region, an effective fluid is believed to enter into a surface chemical reaction with the metal being cut to produce a low shear strength metal salt. The frictional resistance is considerably lowered if metal-to-metal contact is reduced by the formation of such a metallic compound between the sliding surfaces. Thus, it is believed that the alternating properties here displayed by the alcohol–aluminum combination is a chemical phenomenon.

Acknowledgment.—The writer wishes to acknowledge the coöperation of the staff members of the Applied Science Research Laboratory of the University of Cincinnati and of the Research Laboratory of the Cincinnati Milling Machine Company.

Summary

An alternation in the cutting force required to remove a chip from an aluminum block at very low cutting speed is noted when successive normal, primary, monohydric alcohols are used as cutting fluids. Alcohols having an odd number of carbon atoms require lower cutting forces than the compounds having an even number of carbon atoms.

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CLEVELAND, OHIO RECEIVED JULY 12, 1944

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF UNIVERSAL OIL PRODUCTS COMPANY]

Effects of Temperature, Contact Time, and Water Vapor on the Olefin–Aromatic Ratio in the Dehydrogenation of *n*-Heptane with Chromia–Alumina

BY WILLIAM J. MATTOX

Some of the more recent publications[1-8] on the aromatization of aliphatic hydrocarbons have contained discussions relative to the formation of olefins and their role in the mechanism of the cyclization reaction. In most instances with chromia-containing catalyst where the corresponding olefin yields have been reported, the olefin–aromatic ratio in the reaction products decreases with increased contact time. With the exception of comparatively short contact times, the ratio is usually less than 1. For example, the data of Pitkethly and Steiner,[3] obtained at 475°, show olefin–aromatic ratios greater than 1 only at contact times of less than about nine seconds.

In connection with work reported previously,[9] and to some extent as observed in the published work of others,[3,10] variations in certain conditions under which the aromatization reaction may be carried out were observed to influence the proportion of olefins in the recovered products. Taylor and Turkevich[11] observed that water vapor, which is strongly absorbed by chromium oxide gel, is a marked poison for the aromatization reaction. Salley, Fehrer and Taylor,[12] in studying the addition of water vapor in 0–3 mole per cent., state that the retardation effects involve a decrease of toluene, but not of olefins. The highest olefin–aromatic ratio calculated from the data reported by these investigators, however, is 0.43.

The present paper constitutes a summary of a more extensive investigation of some of the effects of temperature, contact time or space velocity, and water vapor at atmospheric pressure. The

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[1] Goldwasser and Taylor, THIS JOURNAL, **61**, 1766 (1939).

[2] Hoog, Verheus and Zuiderweg, *Trans. Faraday Soc.*, **35**, 993 (1939).

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[9] Grosse, Morrell and Mattox, *Ind. Eng. Chem.*, **32**, 528 (1940); reprinted in Universal Oil Products Co. Booklet No. 241.

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TABLE I

DEHYDROGENATION OF *n*-HEPTANE WITH 8% Cr_2O_3–92% Al_2O_3

Atmospheric pressure, no added water.

Space velocity	Contact time, seconds	Reaction period, hours	Vol. of catalyst, cc.	Grams C_7H_{16} charged	Yield, wt. % of charge					
					Toluene	Heptene	Paraffins[a]	Gas	Carbon	Unaccounted
					500°					
0.63	5.3	1	72	31.0	27.6	13.6	51.2	6.9	1.5	+0.8
3.60	1.4	1	72	177.2	11.9	11.3	75.4	1.7	0.2	+0.5
7.25	0.70	1	20	99.2	6.4	11.6	80.8	2.0	.1	+0.9
20.00	0.272	1	20	273.5	1.7	6.4	90.9	0.9	.03	−0.1
					550°					
0.78	3.2	1	78	41.6	53.7	10.9	15.9	16.5	3.2	+0.2
5.00	0.73	1	20	68.4	16.5	13.0	59.8	11.4	0.7	+1.4
39.80	0.12	1/2	10	136.1	2.2	7.2	85.6	4.4	.08	−0.5
80.00	0.066	1/2	5	136.8	1.0	5.2	92.2	1.5	.06	−0.04
					600°					
1.30	1.93	1	78	69.3	52.3	5.4	9.7	22.6	3.6	−6.4
39.60	0.11	1/2	10	135.4	6.5	8.3	65.0	17.0	0.4	−2.8
80.00	0.056	1/2	5	136.8	3.2	7.4	80.1	8.4	.2	−0.7
160.00	0.030	1/2	2.5	136.8	1.2	5.4	89.2	3.9	.07	−0.2

[a] Unreacted *n*-C_7H_{16} except for small amounts of lower boiling hydrocarbons formed at low space velocities.

effects of pressure constitute a separate investigation.

Experimental

Apparatus and Procedure.—The apparatus and procedure used in this investigation were essentially the same as those described previously for the aromatization of *n*-heptane.[9] For tests in which water was added to the reactants by dehydrating ethyl alcohol, 35 cc. of grade A activated alumina was supported in the 400 to 425° section of the preheater by means of quartz chips. A second layer of quartz chips above the alumina served to preheat the heptane–alcohol charge to the desired temperature. This arrangement, when the chromia–alumina catalyst was replaced by quartz chips, produced no changes in the heptane at the temperatures and space velocities employed in the dehydrogenations.

For the direct introduction of water into the hydrocarbon charge, a second pump of the type described previously[13] was used. In this operation distilled water, together with the heptane, was fed into the upper portion of the preheating section.

The C_7 hydrocarbon fractions, separated from any minor amounts of light or heavier hydrocarbons by distillation, were analyzed by means of bromine number and specific dispersion determinations,[14] in some cases supplemented by acid absorption.

Contact time was calculated by dividing the volume of the free space in the catalyst zone by the mean rate of flow of gas per second corrected to the temperature of the reaction tube. Space velocity as used refers to volumes of liquid feed (20°) per hour per volume of catalyst space.

Materials.—Freshly distilled *n*-heptane obtained from the California Chemical Company was used without further purification. Because of the low solubility of water in heptane, no special drying precautions were undertaken.

For the introduction of water vapor derived from alcohol, absolute ethyl alcohol was mixed with *n*-heptane in the percentages calculated to yield the desired proportions of water and hydrocarbon when dehydration takes place.

The catalyst was an 8 wt. per cent. chromium oxide–92 wt. per cent. alumina composite, prepared from chromium trioxide and gamma alumina by the general method described by Grosse, Morrell and Mattox,[9] calcined in air and reduced for ten to fifteen minutes with hydrogen at 550° before use. A fresh portion of catalyst was used for each test.

Discussion

Dehydrogenation tests were conducted at atmospheric pressure over a range of liquid hourly space velocities of 0.63 to 160, contact times of 5.3 to 0.03 seconds, and at temperatures of 500, 550 and 600° using *n*-heptane without added water vapor. Tests with added water vapor derived from alcohol, in which the water–heptane mole ratio was varied from 0:1 to 1:1, were made at 550° and a hydrocarbon space velocity of approximately 2. The dehydrogenation was also carried out in the presence of water introduced, in regulated amounts, directly into the heptane feed.

Contact Time.—Data for the dehydrogenation of *n*-heptane at temperatures of 500 to 600° are shown in Table I and, graphically, in Fig. 1 as a correlation of heptene–toluene weight ratio and contact time for each of the temperatures investigated. The most pronounced effects of contact time were obtained at values of less than about one second. As the contact time was decreased below one and one-half seconds at 500°, one-half second at 550°, and 0.15 second at 600° the olefin–aromatic ratio increased rapidly from about 1 to a value of about 5. Further increases in this ratio, which could probably be effected by additional decreases in contact time, were not attempted due to the low conversions, 6–8 wt. per cent. of the heptane charge per pass.

The olefin production rates, grams of heptene per 100 g. of catalyst per hour, increased with decrease in contact time and at 600° a value of 644 g. was reached. The relationship of contact time and production rate at each of the tem-

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(13) Tropsch and Mattox, *Ind. Eng. Chem.*, **26**, 1338 (1934); Mattox, U. S. Patent 2,254,539, Sept. 2, 1941.

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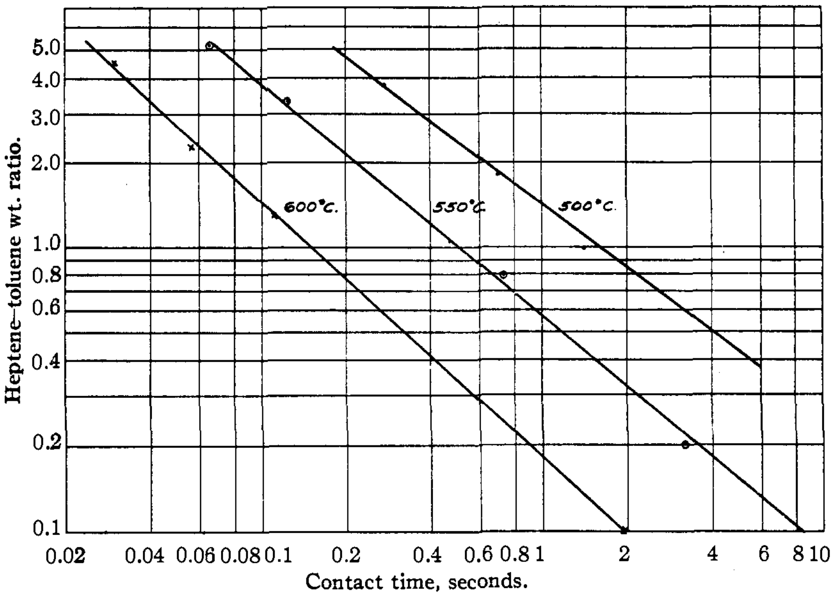


Fig. 1.—Effect of contact time on heptene–toluene ratio.

peratures investigated is shown in Fig. 2. Apparently at long contact times, production rate is decreased by increases in temperature. As contact time is decreased, production rate flattens off, this flattening coming at a longer time and lower rate the lower the temperature, so the largest possible production rate increases with temperature.

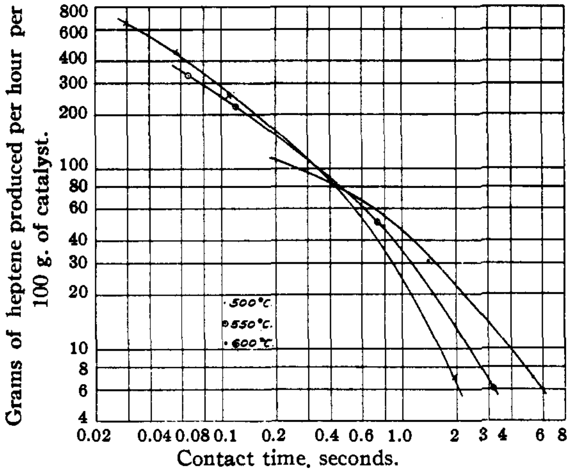


Fig. 2.—Effect of contact time on olefin production rate.

Temperature.—Increasing the reaction temperature at constant contact time resulted in a decrease in the olefin–aromatic ratio, the decrease being more pronounced at the lower contact times. At 0.2 second the 95° increase between 495 and 590° decreased the ratio from 5:1 to 1:1 whereas at 0.1 second an increase of 80° caused the same change in ratio. At each temperature investigated, however, ratios of 4 to 5 were obtained with contact times between 0.02 and 0.2 second.

The olefin–aromatic portion of the dehydrogenation products obtained at 550° and 80 liquid hourly space velocity (0.07 second) contained 84% heptene. The effects of temperature as a function of contact time for heptene–toluene ratios of 1 to 5 are shown in Fig. 3.

Water Vapor.—Dehydrogenations carried out in the presence of 0, 0.25, 0.50 and 1.0 mole of water vapor (derived from alcohol) per mole of heptane are summarized in Table II. The effects of 0.25–1.0 mole of water, as compared to the test in which none was added, are shown graphically in Fig. 4 as a correlation of heptene–toluene yields and mole ratio of water or alcohol added. As the proportion of water was increased, the aromatic yield rapidly decreased and the olefin increased so that on addition of 0.5 mole or more per mole of heptane, the yield of olefin exceeded that of the aromatic. With 1 mole of water per mole of hydrocarbon charge, the heptene yield was increased to 28.9% of the heptane decomposed The addition of this quantity of water decreased the heptene yield per pass to 6.1% as compared to 10.5% without water.

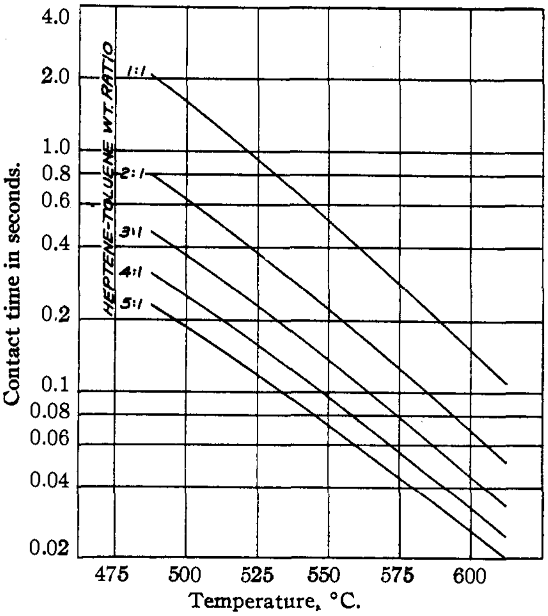


Fig. 3.—Effects of temperature on heptene–toluene ratio.

The direct addition of 0.38 mole of distilled water to each mole of the heptane charge at 550° and hydrocarbon space velocity of 2 resulted

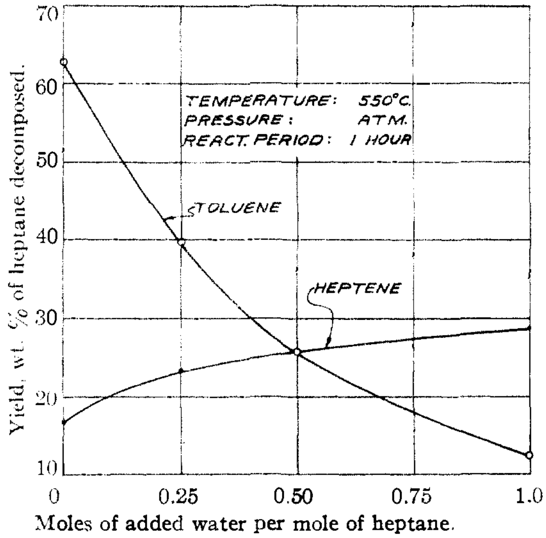


Fig. 4.—Effects of water vapor on heptene–toluene ratio (water derived from alcohol).

in a 13.5 wt. per cent. yield of heptene and 2.9% of toluene per pass. As weight per cent. of the heptane decomposed, these yields correspond to 67% of the olefin and to 14% of the aromatic, indicating that water introduced directly may be more effective for increasing the olefin–aromatic ratio than the use of alcohol. The ethylene derived from the added alcohol may have some influence on the reaction, although Taylor and Fehrer have shown[10] that the simultaneous presence of hydrogen suppresses the poisoning effects of ethylene on chromium oxide catalyst in the dehydroaromatization of n-heptane.

Other factors such as catalyst composition or variations in activity of dehydrogenating oxides or their composites also affect the ratio of the products formed, although these are not included as a part of this investigation.

Efficiency of Olefin Production.—Some effects of the variables investigated on the efficiency of heptene production are summarized in Fig. 5 as a correlation of heptene yield per pass and per cent. heptane decomposed. In the absence of added water vapor the heptene yields were at all conversions increased by a decrease in temperature. At 500° the yields were only slightly higher than at 550° but considerably above those obtained at 600°. Water vapor introduced by dehydration of ethyl alcohol tended to decrease the efficiency of olefin formation although the direct addition of water resulted in the highest ultimate yield of heptene which at 10% conversion amounted to 90% as compared to 69% at 500° without water. The corresponding yields at 20% conversion were 67 and 54%.

TABLE II

DEHYDROGENATION OF n-HEPTANE IN THE PRESENCE OF WATER DERIVED FROM ALCOHOL

Temperature, 550°; pressure, atm.; reaction period, 1 hour; volume of catalyst, 100 cc.

Space velocity[a]	1.98	1.96	2.00	2.02
n-C_7H_{16} charged, g.	135.4	134.0	136.8	138.1
Mole ratio of added H_2O:moles H_2O/mole C_7H_{16}	0	0.25	0.50	1.0
Yields: wt. % of charge				
Toluene	39.2	14.7	7.0	2.6
Heptene	10.5	8.6	7.0	6.1
Heptane	37.4	63.1	72.9	78.9
Hcbns. boiling below 85°	2.7	3.0	3.5	3.7
Gas (cor. for added C_2H_4)	7.8	8.0	7.0	6.5
Carbon	1.93	1.58	1.32	0.85
Unaccounted	−0.5	−1.0	−1.3	−1.3
Yields: wt. % of heptane dec.				
Toluene	62.6	39.8	25.8	12.3
Heptene	16.8	23.3	25.9	28.9
Mole % of H_2 in gas[b]	92.9	79.4	51.5	33.9
Mole % of olefins in gas	0.5	10.5	27.1	44.9

[a] Based on n-C_7H_{16}. [b] Gas contains C_2 hydrocarbons from alcohol.

Acknowledgment.—Appreciation is expressed to Messrs. M. W. Cox and J. E. Kidder for assistance in the experimental work.

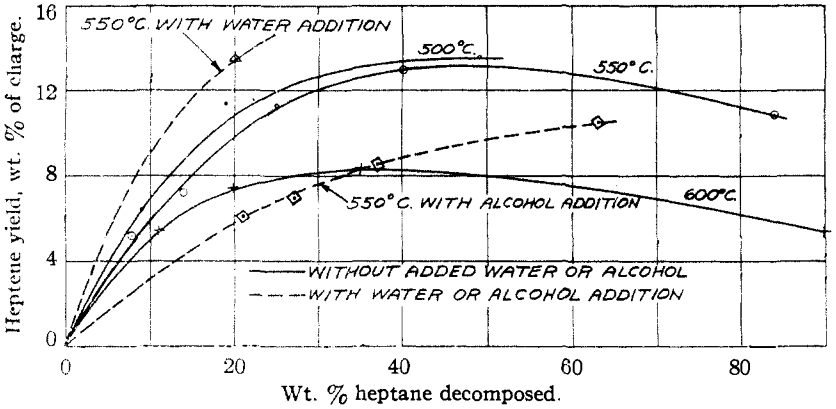


Fig. 5.—Effects of variables on efficiency of heptene production.

Summary

Variations in the ratio of olefins to aromatics produced in the dehydrogenation of n-heptane with chromia–alumina as influenced by temperature, contact time or space velocity, and water vapor have been described.

With contact times below about 1.5 second at 500°, 0.5 second at 550° and 0.15 second at 600° the dehydrogenation products contained a greater proportion of heptene than of toluene. Longer contact times, at the corresponding temperatures, resulted in a predominance of the aromatic.

The effects of temperature were as pronounced as those of contact time on olefin–aromatic ratio. At a given contact time, increases in temperature resulted in decreases in the ratio, the rate of decrease being somewhat higher at the lower contact times.

Addition of water vapor, by dehydration of ethyl alcohol, in ratios of 0–1 moles per mole of heptane, preferentially retarded the formation of aromatics so that with 0.5 mole or more per mole of heptane the olefin–aromatic ratio was greater than 1. Under the more favorable conditions found in the direct addition of water, a ratio of 4.8 was obtained with a total olefin–aromatic conversion of 16.4 wt. per cent. of the charge per pass; the toluene–heptene yield amounted to 82% of the heptane decomposed.

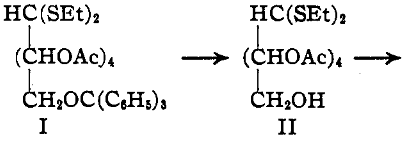
CHICAGO, ILLINOIS RECEIVED APRIL 24, 1944.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Ring Closure Studies in the D-Glucose Structure

BY M. L. WOLFROM, S. W. WAISBROT, D. I. WEISBLAT AND A. THOMPSON[1]

In the D-galactose structure, Micheel and coworkers[2] have synthesized derivatives containing the 1,6 or heptanoside ring. The best starting point for these important syntheses was the tetraacetate (I) of the 6-triphenylmethyl (trityl) ether of D-galactose diethyl mercaptal,[3] from which D-galactoheptanose pentaacetate (IV) was obtained by the step-wise removal of the ether and thioacetal groups on the terminal positions of the D-galactose molecule with subsequent acetylation.



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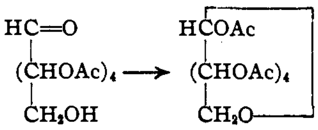

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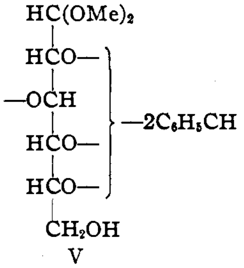

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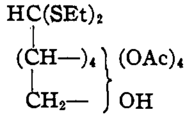

IIa

The initial derivatives corresponding to I and II in the D-glucose structure have not hitherto been available because of crystallization difficulties. We have now succeeded in synthesizing the 6-triphenylmethyl ether of D-glucose diethyl mercaptal tetraacetate, from which a crystalline D-glucose diethyl mercaptal tetraacetate (m. p. 117°; spec. rot. −25°, $CHCl_3$, D line) was obtained on removal of the triphenylmethyl group with dilute acetic acid according to the procedure of Kuhn and co-workers.[4] Previously reported work[5] from this Laboratory conclusively demonstrates that D-glucose diethyl mercaptal tritylates in the sixth position. Thus structure I is assured for the triphenylmethyl ether of D-glucose diethyl mercaptal tetraacetate. The same diethyl mercaptal tetraacetate (m. p. 117°; spec. rot. −25°, $CHCl_3$, D line) was obtained by mercaptalation of D-glucose 2,3,4,6-tetraacetate. If no acetyl migration had occurred, the 2,3,4,5-tetraacetate should have been obtained from I and a different 2,3,4,6-tetraacetate from D-glucose 2,3,4,6-tetraacetate. Since the two products were alike, it is apparent that an acetyl migration had occurred and the position of the unsubstituted hydroxyl group in this D-glucose diethyl mercaptal tetraacetate (IIa) is unknown. A similar shift is known[6] to occur when D-glucopyranose tetrabenzoate is mercaptalated. Evidence was obtained in this case that the isolated reaction product, also formed by the mercaptalation of D-glucofuranose pentabenzoate, carried the unsubstituted hydroxyl on carbon two of the D-glucose chain.[6a]

Demercaptalation of the D-glucose diethyl mercaptal tetraacetate with mercuric chloride and cadmium carbonate in moist acetone[7] led to the isolation of the ethyl α-thio-D-glucoside tetraacetate of Schneider and Sepp.[8] A furanoside structure for the parent, unacetylated substance has been favored[8b,9] but not rigorously proved. The substance was accordingly subjected to periodate oxidation.[10] If a furanoside ring were present, the substance would oxidize uniquely to

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[1] Research Foundation Postdoctoral Fellow of the Graduate School.

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